

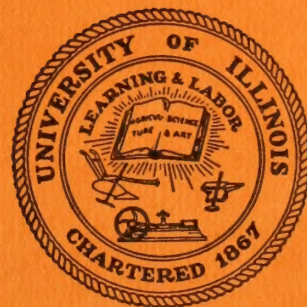
# **ENVIRONMENTAL POLLUTION BY LEAD AND OTHER METALS**

**NSF RANN GRANT GI-31605**

**Progress Report**

**November 1, 1972 to April 30, 1974**

**University of Illinois at Urbana-Champaign  
INSTITUTE FOR ENVIRONMENTAL STUDIES**





Experimental findings and conclusions should be regarded as tentative and should not be cited, reproduced, or included in other publications without the express approval of the project director.

AN INTERDISCIPLINARY STUDY  
OF ENVIRONMENTAL POLLUTION  
BY LEAD AND OTHER METALS

Sponsored by  
NATIONAL SCIENCE FOUNDATION  
RANN GI-31605

INSTITUTE FOR ENVIRONMENTAL STUDIES  
University of Illinois  
at Urbana-Champaign

Progress Report (PR4)\*

November 1, 1972 to April 30, 1974

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## I. INTRODUCTION

This is an 18-month progress report of the University of Illinois Metals Task Force research program for the period November 1, 1972 to April 30, 1974. Included are major reports from the ecosystem, soil-water-air-plant, modeling, and analytical laboratory teams and a termination report from the animal processes team. In addition to this comprehensive document, a summary report of this material has also been prepared and is available.

### History and Organization

The concept of a wide-scale interdisciplinary project on environmental contamination by lead originated in 1968 with Professors R. L. Metcalf and Ben B. Ewing. Considerable discussion with interested faculty resulted in the formulation of a preliminary proposal for an exploratory and planning grant from the National Science Foundation IRRPOS program. A grant for the period July 1, 1970 to October 31, 1971 was received and the project began to evolve. Initially conceived as a mixed multidisciplinary-interdisciplinary project the team has evolved into a true interdisciplinary team.

Since the initial exploratory and planning grant, two additional grants from the National Science Foundation RANN



program have been received for continuation of these studies.

The current organization of the Metals Task Force is shown in Figure 1. Professor H. A. Laitinen is the principal investigator and Director of the Metals Task Force, and Professor G. L. Rolfe is the co-principal investigator and Associate Director. Professor Rolfe also serves as research coordinator for the project and team leader for the ecosystem team. Professor D. E. Koeppe is the team leader of the soil-water-air-plant (SWAP) team and Professor J. L. Hudson is team leader of the modeling team. The Analytical laboratory is directed by Professor A. M. Hartley. George Provenzano carries out the economics and social sciences phases of the research.

Although the project is oriented toward research, there is an important educational component as well. Six students have received their Ph.D. degrees presenting theses with a substantial component of research relevant to the project. An equal number have received MS degrees. Over a dozen post doctoral associates have worked on the project since its inception and approximately 40 research assistants have been employed. The students have received valuable job experience in the environmental sciences area and in their specific disciplines.

## Objectives

The major objectives of the Metals Task Force research program include the development of interdisciplinary research methods on a university campus and an evaluation of the input, distribution, and effects of lead in the environment. This latter objective includes studies of the current distribution of lead in ecosystem components resulting from the use of lead in gasoline and studies designed to assess the fluxes, factors controlling fluxes, and the effects of lead on ecosystem components other than man. Much of this research is nearing completion and the results have provided considerable insight into the lead problem through models developed using project data and have identified several major problem areas not adequately researched to date. These include definitive studies on lead effects on aquatic and terrestrial plant productivity and studies of the sources, transport pathways, and forms of lead in the urban environment.

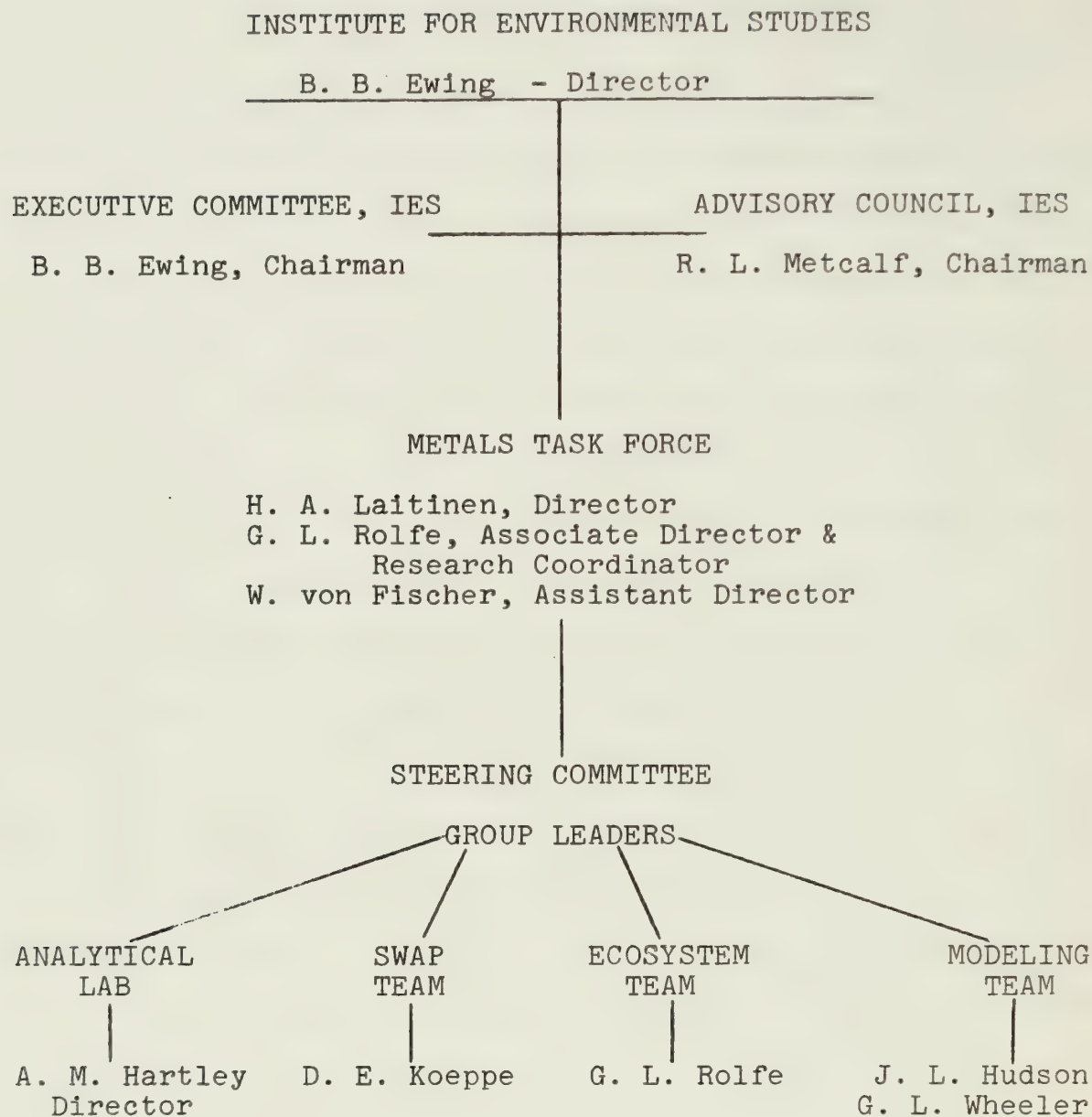


Figure 1

Project Organization



## II. Ecosystem Studies

G. L. Rolfe

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The system under study by the Illinois team is an 86 square mile ecosystem based on a watershed located in central Illinois. The watershed lies primarily to the north of Champaign-Urbana and is predominantly rural, agricultural in nature. However, the watershed also includes approximately 90% of the cities of Champaign and Urbana with approximately 100,000 inhabitants and thus does include a significant urban component. Major crops of the rural area are corn and soybeans. Woodlands, pasture, and wasteland such as railroad right of ways and stream margins are also included in the watershed area.

The rural portion of the watershed is drained by the Saline Branch of the Vermillion River and the urban portion by the Boneyard Creek. The streams join on the east edge of Urbana and flow out of the system to the east.

The objectives of the Illinois study include characterizing the input, accumulation, and output of

lead from automobile sources in a typical midwestern ecosystem, understanding the mechanisms controlling fluxes between system components and evaluating potential effects of lead on ecosystem components other than man. These data provide critical baseline data previously not available and valuable for evaluating the short and long term impact of the use of lead in gasoline.

#### Ecosystem Inputs

Gasoline consumption represents the major source of lead input to the watershed. In order to monitor this input, a traffic monitoring network was established in 1971 to monitor spatial and temporal variations of traffic volume and thus lead input. Urban and rural traffic volume studies have been completed and data analysis is nearing completion.

Traffic volume data were converted to gasoline consumption with the following assumptions:

1. 2.5 grams of lead/gallon of gasoline
2. In urban areas 50% of the consumed lead is emitted from the exhaust system.
3. In rural areas 80% of the consumed lead is emitted.

These assumptions are reasonable in view of data presented

by Hirschler and Gilbert, 1963 which show only 21 to 28% of total lead in gasoline to be retained by the automobile during average driving studies.

Current lead inputs based on the traffic monitoring data and the above assumptions are shown in Table 1. On a daily basis the input averages 79 kg/day with 73% of these emissions being in the urban compartment. The yearly total lead emissions into the ecosystem are approximately 29,000 kg. If the average lead content per gallon of gasoline is considered to be 2.0 g the daily input is approximately 63 kg using the same percent emission figures as above. These emission data on a per vehicle mile basis are .101 g and .128 g respectively for the urban and rural compartments. These figures compare favorably with the average lead emission rate for production vehicles of .108 g/mile of Cantwell et al., 1972. If Cantwell's figure of .050 g remaining airborne or 46% of the total is used we find that the total input of lead to ecosystem components with the exception of the air is reduced to 16,000 kg per year. The majority of this deposition occurs in the urban area and along major highways.

Projections of annual growth rate of traffic volumes have been made for the urban area considering five zones



Table 1

## Lead Inputs from Automobile Emissions

<u>Compartment</u>	<u>Total Daily Vehicle Miles</u>	<u>Gallons Total Daily Gas Consumption</u>	<u>Grams Total Daily Lead Emissions</u>
Rural	164,000	10,520	21,000
Urban	576,000	46,050	58,000
Totals	740,000	56,570	79,000

based on traffic volume as shown in Table 2. Average daily traffic volumes for the past 15 years are plotted in Figure 2 for each of these road classes and show a linear relationship although long-term trends of vehicle-mile growth are known to be nonlinear. Figure 3 depicts the overall growth rate in each of these classes through 1980.

From the average curves the following annual growth rates have been computed:

Class I	2.5%
Class II	3.3%
Class III	3.1%
<u>Class IV</u>	<u>1.9%</u>
Overall	3.1%

Rural growth rates are currently being estimated but the growth rate for Class IV urban streets of 1.9% is expected to be similar.

These traffic volume growth rate figures are being used in the ecosystem modeling studies to provide a basis for estimating future system inputs.

Inputs based on traffic monitoring estimates are being compared to a limited extent with air monitoring and lead deposition data currently being taken. This comparison allows a check of the traffic monitoring method

Table 2  
Traffic Volume Ranges by Class

	<u>Average Daily Traffic</u>
Class I	Over 10,000
Class II	5,000 to 10,000
Class III	2,500 to 4,999
Class IV	1,000 to 2,499



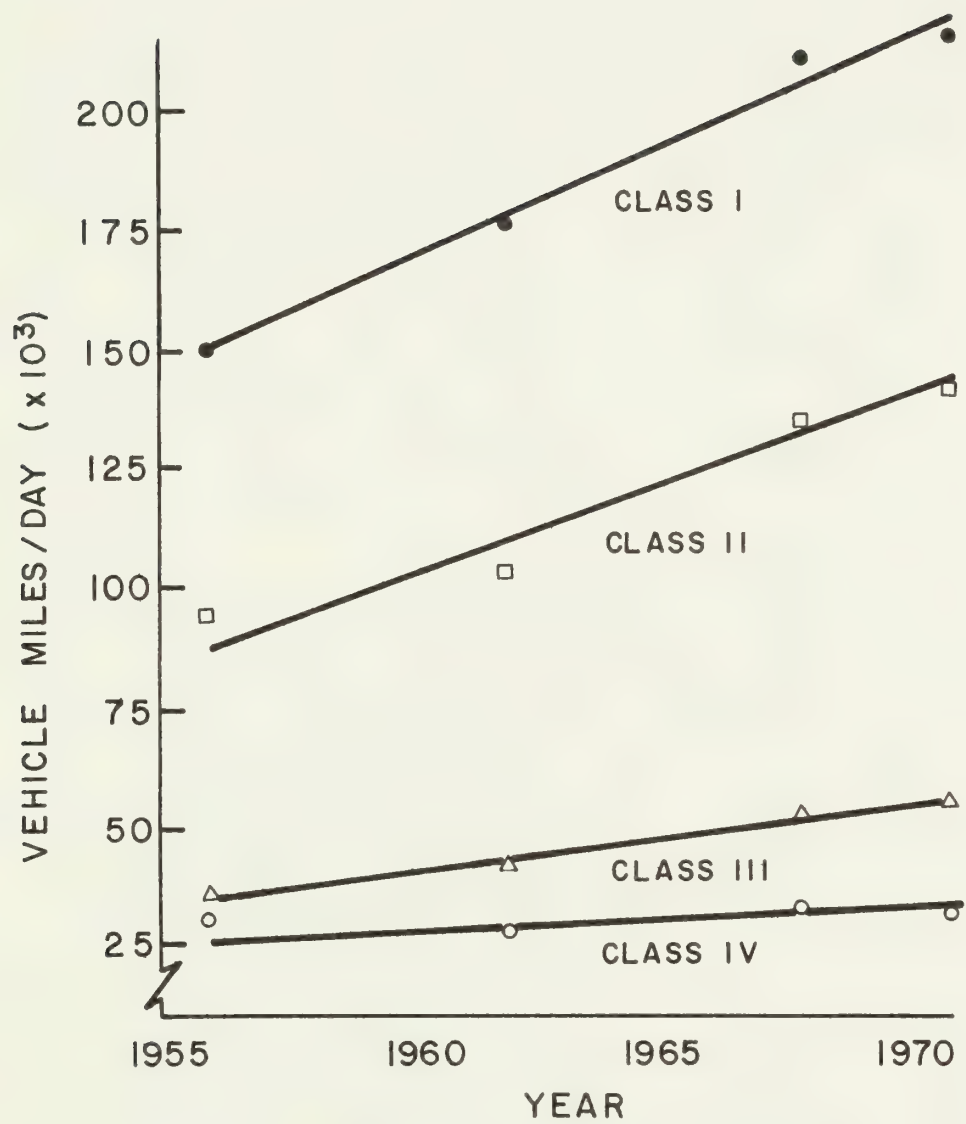


Figure 2 . Traffic Growth on Urban Streets, by Class

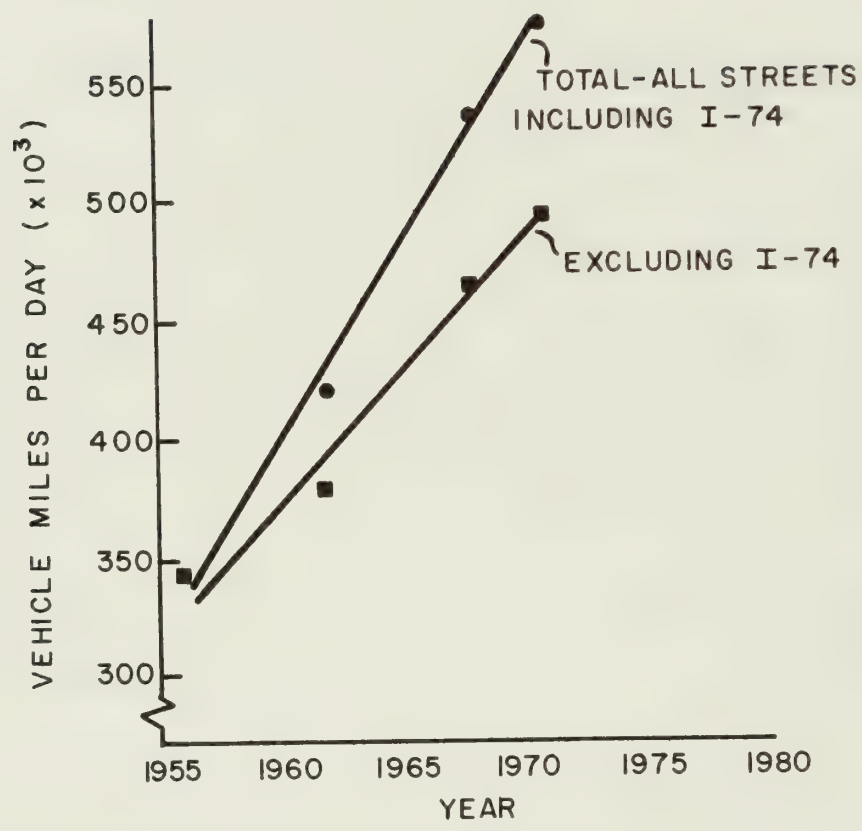


Figure 3 . Overall Traffic Growth on Urban Streets

of determining system lead inputs. An additional rough check was made by comparing average lead emissions per vehicle mile with those reported in the literature and found to be favorable (Cantwell et al., 1972).

The input of lead to the ecosystem in rainwater has also been monitored for the past 18 months and is shown in Figure 4. Input associated with rainfall averages 2% of the total input from automobile emissions. Collections were made by placing 48 acid washed polyethylene bottles at random locations within the watershed to collect samples during each storm period. Total rainfall was monitored using recording rain gages.

#### Air Monitoring

The field sampling program encompassed two types of preliminary investigations. One study focused on measuring the distribution of ambient lead levels, particle size distribution, and deposition rates in and near the rural section of the ecosystem while the other study examined these variables in the urban compartment. Each of these studies will be discussed separately.

#### Rural Study

The rural study utilized eight General Metals Works high volume samplers for making field measurements. In order to utilize these field instruments in the most

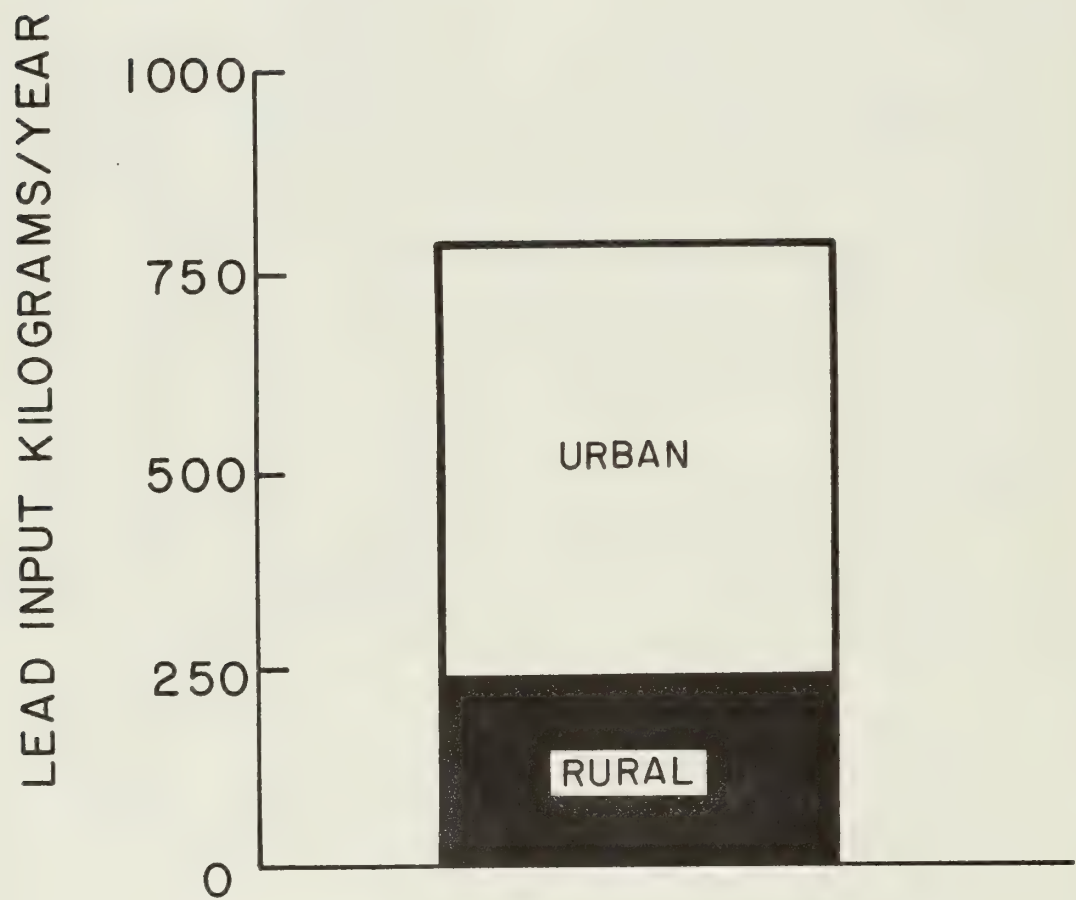


Figure 4 . Lead Input in Rainfall



effective way, an analytical model was used for locating the samplers. From the concentration distributions predicted by the model, the high volume samplers were placed to most effectively test the model. The location of the samplers is given in Figure 5.

The high volume samplers were powered by electrical outlets utilizing either existing power outlets in the field or propane fueled electrical generators. Gelman 8"x10", GA-1 Metrical triacetate filters ( $5\mu$  pore size) were initially used as primary filters with standard 8"x10", type A, fiberglass filters ( $.8\mu$  pore size) used for back-up secondary filters. Both filters were analyzed for lead content. It was found that utilizing a single 8"x10" fiberglass filter gave equivalent results to those obtained using the dual filter arrangement and the single filter was used in subsequent tests.

The flux of lead particulates was measured using a modified dust fall station. A polyethylene canister, 10 inches in diameter, and 12 inches deep, was mounted 3 feet off the ground. Additional canisters were placed in the ground so that the canister lip was three inches off the ground. The canister was filled with an isopropyl alcohol solution with a known lead blank. The level in

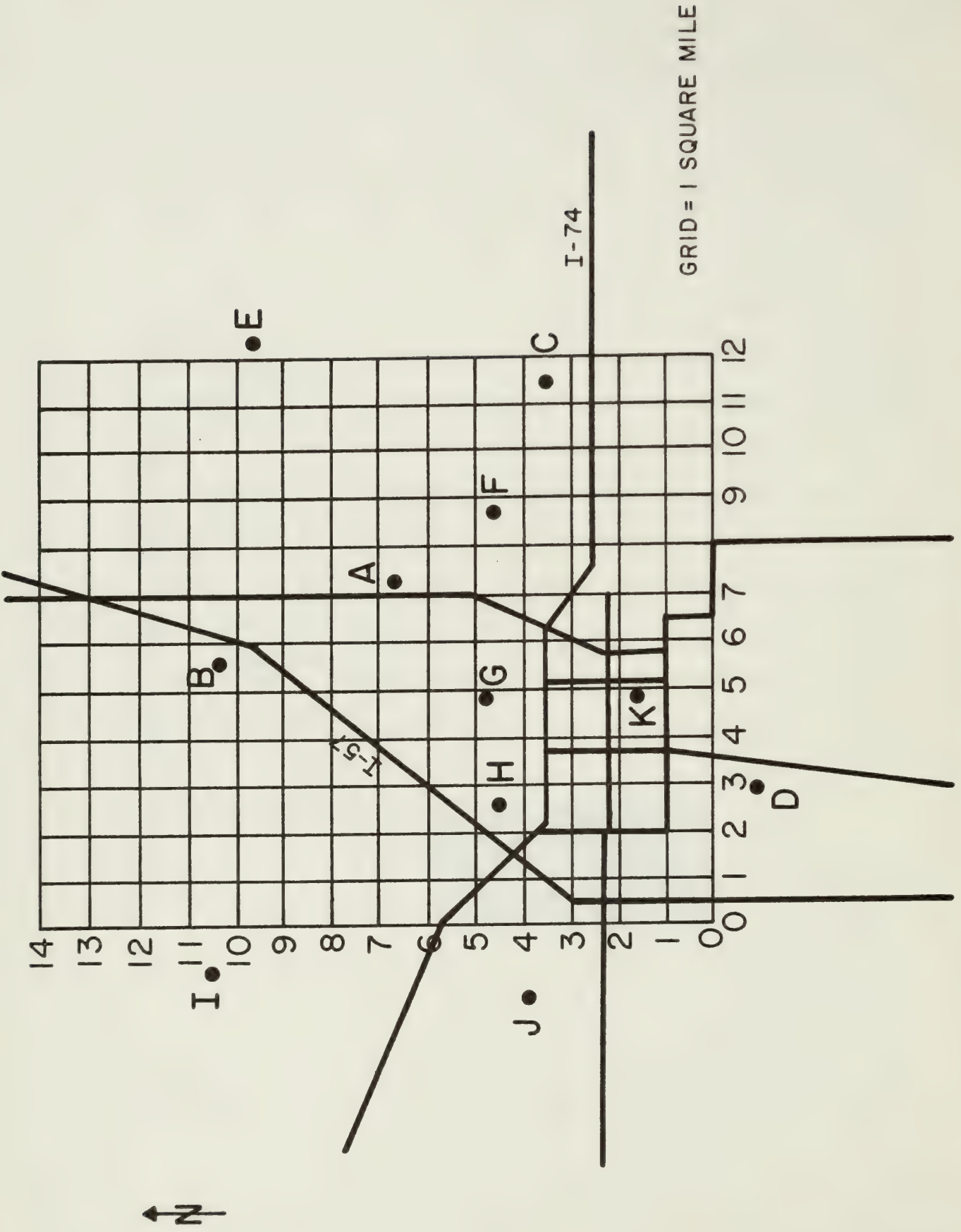


Figure 5 . Air Sampling Locations

the canister was maintained constant at a depth of 1 inch. Deposition measurements were made over a period of 30 days. Each canister was fitted with a tight fitting lid to ensure no loss of fluid during transportation.

### Urban Study

A study to determine the ambient lead particulate concentration and deposition levels in the community of Champaign-Urbana, Illinois, has recently been undertaken. To date, four sampling stations are in operation. Two stations are located in a suburban section of the community (Stations D and H on Figure 5), while the remaining two stations are located near the center of the University of Illinois at Urbana campus, at the Roger Adams Laboratory Building (Station K, Figure 5). One campus station is located in front of the laboratory, while the other is on the roof of the four-story building. Total lead particulates, particle size distribution and deposition measurements are being made at all four stations. The sampling techniques for each of these measurements are the same as for the rural area discussed earlier.

### Results

Total atmospheric lead concentrations were measured for twenty-four periods on twelve days, of which three were

in August, two in September, and seven in October, 1973. Averages over these twelve days are shown in Table 3 for the eleven sampling stations. There is not a large variation in lead concentration throughout the rural portion of the ecosystem.

At the remote stations E and I, the lead concentration averages about  $0.22 \mu\text{g}/\text{m}^3$  whereas nearer Champaign-Urbana, but still in the rural area, the average is about  $0.30 \mu\text{g}/\text{m}^3$ . In the suburban area, the average lead concentration is about  $0.43 \mu\text{g}/\text{m}^3$  and the one ground-level urban site indicates an average of  $0.61 \mu\text{g}/\text{m}^3$ .

It is seen, then, that although Champaign-Urbana makes some contribution to the total lead concentration in the rural air, most of the lead in the air comes from other sources.

Particle size distribution in the rural area was also measured using an Anderson particle sizing head. No results are presently available.

Some data were obtained on the dependence of total lead concentration with height in the urban area. The average lead concentration is  $0.61 \mu\text{g}/\text{m}^3$  at ground level and  $0.54 \mu\text{g}/\text{m}^3$  at fourth-floor rooftop level.

Soil deposition data are shown in Table 4.



Table 3  
 Comparison of Model and Field Data  
 Three-Month Averages  
 Lead in Air  $\mu\text{g}/\text{m}^3$

<u>Site</u>	<u>Measured</u>	<u>Predicted</u>
A	.30	.26
B	.31	.25
C	.28	.25
E	.23	.23
F	.31	.27
G	.29	.28
I	.22	.24
J	.28	.26
D	.45	Model Not Applicable
H	.42	Model Not Applicable
Roger Adams Lab	.61	Model Not Applicable

Table 4 . Pb in Dustfall  $\text{mg/m}^2\text{-mo}$ 

Area	Number of Sites	Mean	Standard Deviation of Data( $\sigma$ )
Rural	6	1.40	.264
Suburban	3	2.16	
Urban	2	2.32	
All	11	1.82	.636

### System Outputs

Surface drainage discharge has been monitored continuously at five stream gaging stations located on the Saline Branch of the Vermillion River and the Boneyard Creek (Figure 6). The five gaging locations allow a comparison of the water volume and lead output from the rural portion of the watershed with outputs from the urban area. This comparison can be made between a small rural agricultural watershed of approximately 4 square miles and a similar size totally urban watershed or between the entire rural and urban compartments. An additional gaging station is located 5 miles downstream from the watershed and allows an estimate of stream recovery due to dilution effects of rural drainage waters.

Total water volume moving past each gage is determined for each 24-hour period. This time period corresponds with the water sampling period. Continuous duty, compositing water samplers are in operation at each location. Samples are taken at 15-minute intervals and composited for each 24-hour period. During storm periods, a separate automatic water sampler collects individual 1-liter samples at shorter time intervals proportional to stream height.

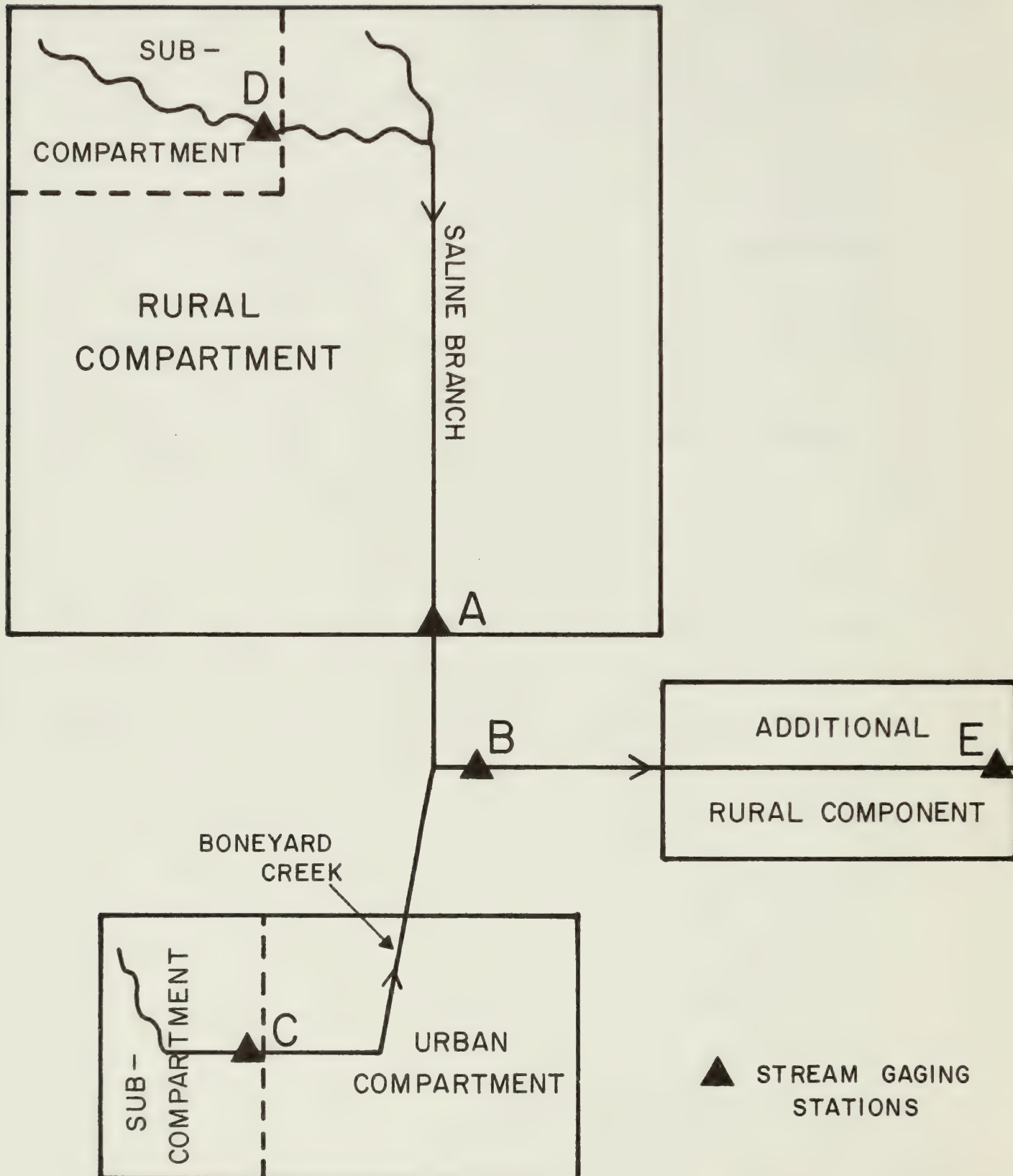


Figure 6. Location of Stream Gaging Stations



The water samples are filtered using a .45 micron Millipore filter. The filtrate is analyzed by Anodic Stripping Voltammetry and the suspended solids by Atomic Absorption Spectroscopy. The concentrations are widely variable, ranging from 0 to 15 ppb in the filtrate to 15 to 200 ppb in the suspended solids.

The total output of lead on a yearly basis, based on 20 months data, for the urban and rural compartments is shown in Figure 7. The lead output on a yearly basis for the urban compartment is approximately 780 kilograms or 80% of the total lead output. Output from the rural compartment totals 200 kilograms. A comparison between the total output (Figure 7) and the total input of 29,000 kg to the ecosystem demonstrates that only 3% of the total input exits via streamwater. If the input deposition figure of 16,000 kg is used this estimate becomes 6%. Both indicate a considerable accumulation of lead in other components of the system.

In consideration of lead output in streamwater, it is important to evaluate the distribution of lead in the filtrate and suspended solids. Figure 8 illustrates the distribution of lead outputs between filtrate and solids for both urban and rural compartments. As would be

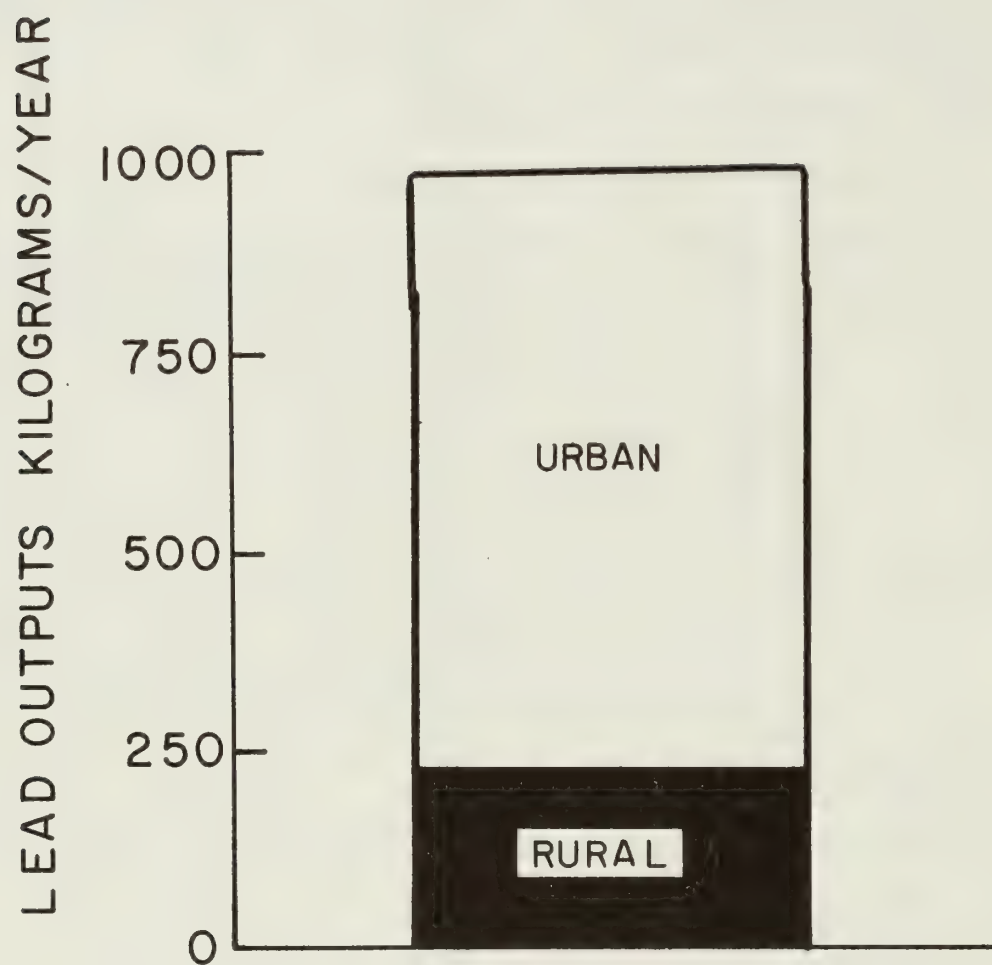


Figure 7. Total Lead Output in Streamwater from Urban and Rural Compartments

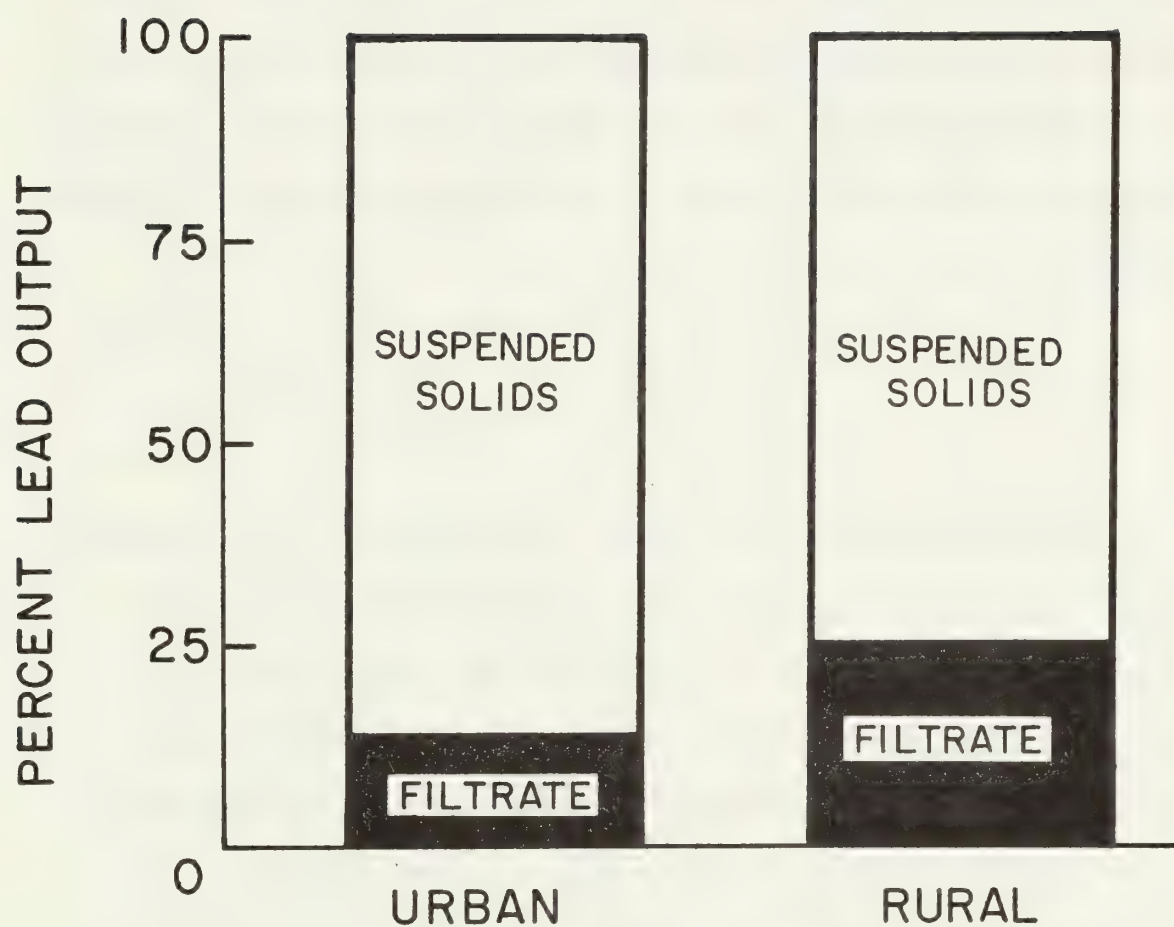


Figure 8. Lead Outputs in Filtrate and Suspended Solids from Urban and Rural Compartments

expected, the majority of lead output is associated with suspended solids in both urban and rural compartments with very little dissolved in the filtrate. The ratio of lead in suspended solids to lead in filtrate varies from 4:1 in the rural compartment to 27:1 in the urban compartment. The large amount of lead associated with suspended solids in the urban compartment directly relates to the vast areas of impervious surfaces in the urban which are quickly washed away during rainfall periods.

Additional comparisons in lead output from completely urban and rural agricultural watersheds using the sub-watersheds delineated in Figure 6 have been made. The urban system contributes almost 93% of the total lead exiting these subcompartments. This would be expected since the agricultural watershed has only a few low traffic volume country roads.

#### Lead in System Components

##### Lead in Soils and Plants

Study of lead in plants and soils was initiated in the summer of 1970. This initial study focused on lead



in six plant species, including corn and soybeans, and the associated soil in transects away from one of the major highways of the watershed (approximately 12,000 vehicles per day). In nearly all species tested, lead in and/or on tissues was a function both of distance from the road and lead in the soil. Plant lead correlations with distance are summarized in Table 5 and with soil lead in Table 6. Analyses of variance were run to determine differences in lead content of taxa and lifeforms (i.e., annual or perennial). No significant differences were found in root lead, but the lifeform-family interaction was significant for lead in washed foliage. Table 7 shows the interpretation of the significant interaction. These data suggest that some plant species accumulate more lead than others and that accumulation rate is not influenced by whether the species is an annual or perennial. The correlation between distance from the highway and soil lead was insignificant over the 200 meter transects examined, although there was a steep drop in soil lead from the highway to approximately 50 meters on the downwind side and to approximately 20 meters on the upwind side with both 0 to 10 cm samples and 10 to 20 cm samples. The correlation between the surface soil (0-10 cm) and the subsurface soil (10-20 cm) was significant ( $P \leq 0.001$ ).

Table 5

Summary of Correlations between Log of Distance from Highway and Lead in Plants. Probabilities Are Based on a "Z" Distribution.

		Correlation Coefficient	Significance ( $P \leq$ )	Percent of Variance Accounted for by Correlation
Corn	root	-0.417	0.0014	17.4
	washed foliage	-0.657	0.0000	43.1
	unwashed foliage	-0.612	0.0000	37.5
Bluegrass	root	-0.424	0.0154	18.0
	washed foliage	-0.674	0.0005	45.0
	unwashed foliage	-0.793	0.0000	63.0
Soybeans	root	-0.094	0.2546	0.9
	washed foliage	-0.727	0.0000	52.9
	unwashed foliage	-0.681	0.0000	46.4
Sweetclover	root	-0.392	0.0051	15.4
	washed foliage	-0.640	0.0000	41.0
	unwashed foliage	-0.668	0.0000	44.7
Fleabane	root	-0.412	0.0020	17.0
	washed foliage	-0.770	0.0000	59.4
	unwashed foliage	-0.722	0.0000	52.2
Dandelion	root	-0.591	0.0089	35.0
	washed foliage	-0.638	0.0054	40.8
	unwashed foliage	-0.792	0.0015	62.8

Table 6

Summary of Correlations between Lead in Soil and Lead in Plants. Probabilities Are Based on a "Z" Distribution.

	Surface Soil (0-10 cm)			Subsurface Soil (10-20 cm)		
	Correlation Coefficient	Significance (P<)	Percent of Variance	Correlation Coefficient	Significance (P<)	Percent of Variance
Corn washed foliage	0.723 0.169	0.0000 0.1335	52.3 2.9	0.449 0.370	0.0010 0.0060	20.1 13.7
Bluegrass washed foliage	0.421 0.680	0.1335 0.0359	17.7 46.3	-0.119 -0.161	0.3520 0.3050	1.4 2.6
Soybeans washed foliage	0.305 0.373	0.0217 0.0136	9.3 13.9	0.324 0.432	0.0150 0.0043	10.5 18.7
Sweetclover washed foliage	0.035 0.248	0.4325 0.1112	0.1 6.2	0.170 0.112	0.2119 0.3015	2.9 1.2
Fleabane washed foliage	0.170 0.322	0.1539 0.0301	2.9 10.4	0.383 0.288	0.0139 0.0548	14.7 8.3
Dandelion washed foliage	0.367 0.641	0.1112 0.0166	13.5 41.1	-0.077 -0.170	0.3974 0.2877	0.6 2.9

Table 7

Analysis of Significant Lifeform-Family Interaction of Lead  
in Washed Foliage Using Tukey's W-Procedure at  $P \leq 0.05$ .

Values Are Mean Lead Levels in ppm Dry Weight Basis. A  
Common Underline Indicates No Significant Difference.

<u>Soybeans</u>	<u>Dandelion</u>	<u>Bluegrass</u>	<u>Fleabane</u>	<u>Sweetclover</u>	<u>Corn</u>
11.4	9.6	8.6	6.8	6.0	6.0
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During the last three years, soils in the watershed were sampled in detail to further elucidate the relationship between traffic volume, distance and direction from highways. Traffic volume estimates were used to classify roads. Sampling was done in transects to 200 meters from road pavements with only the surface soils examined (0-10 cm) in some cases and profiles taken in others. (Table 8). Highest levels were found immediately adjacent to pavements of roads with highest traffic volumes. On the downwind side (east) of north-south roads, the lead content of soils decreased to background levels within 50 meters. On the upwind side of the roads, levels immediately adjacent to the pavement are comparable to those on the downwind side, but decrease more rapidly away from the road reaching background levels within 20 to 30 meters. Roads with low traffic volumes (less than 1,000 vehicles per day) have associated soil lead gradients that are extinct within no more than 15 meters of the pavements on both the upwind and downwind sides. Therefore, we conclude that soil lead is little influenced beyond the right-of-way of roads with less than 1,000 vehicles per day. East-west roads with high traffic volumes had soil lead gradients that were essentially comparable on the north

Table 8

Mean Lead Content (ppm) of 0-10 cm Soils from Transects Away from the Two Extreme Road Classes in the Rural Watershed. Common Superscripts Denote No Significant Differences Within Combined Transects.

Distance in meters from Pavement	High Traffic Volume Roads(N-S) (>12,000 vehicles/24 hrs)		Low Traffic Volume Roads(N-S) (>2000 vehicles/24 hrs)	
	East Transect	West Transect	East Transect	West Transect
1	430 <sup>a</sup>	410 <sup>a</sup>	20 <sup>a</sup>	25 <sup>a</sup>
5	66 <sup>b</sup>	35 <sup>b</sup>	15 <sup>b</sup>	15 <sup>b</sup>
10	45 <sup>c</sup>	25 <sup>c</sup>	15 <sup>b</sup>	16 <sup>b</sup>
15	18 <sup>d</sup>	22 <sup>c</sup>	15 <sup>b</sup>	13 <sup>b</sup>
20	24 <sup>d</sup>	20 <sup>cd</sup>	14 <sup>b</sup>	15 <sup>b</sup>
25	17 <sup>d4</sup>	14 <sup>d</sup>	13 <sup>b</sup>	14 <sup>b</sup>
30	25 <sup>de</sup>	11 <sup>d</sup>	14 <sup>b</sup>	14 <sup>b</sup>
40	17 <sup>de</sup>	12 <sup>d</sup>	15 <sup>b</sup>	14 <sup>b</sup>
50	15 <sup>e</sup>	21 <sup>d</sup>	13 <sup>b</sup>	15 <sup>b</sup>
75	14 <sup>e</sup>	13 <sup>d</sup>	13 <sup>b</sup>	16 <sup>b</sup>
100	14 <sup>e</sup>	17 <sup>d</sup>	14 <sup>b</sup>	13 <sup>b</sup>
125	15 <sup>e</sup>	18 <sup>d</sup>	15 <sup>b</sup>	14 <sup>b</sup>
150	13 <sup>e</sup>	14 <sup>d</sup>	12 <sup>b</sup>	15 <sup>b</sup>
175	14 <sup>e</sup>	13 <sup>d</sup>	13 <sup>b</sup>	14 <sup>b</sup>
207	14 <sup>e</sup>	15 <sup>d</sup>	12 <sup>b</sup>	13 <sup>b</sup>

and south sides and intermediate to the east and west gradients on north-south roads in our watershed. Lead in soil nearest the pavements was much the same as for the north-south roads, but the lead gradient dampened to background within 30  $\pm$  40 meters of the pavement.

We can generalize that the higher the traffic volume the higher the soil lead content and the farther the lead gradient will extend from the highway. Even on the most heavily travelled roads, however, the strong enhancement of soil lead extends only 50-75 meters downwind and 25-40 meters upwind. Extremely high lead levels ( $>50$  ppm) were seldom found in this study beyond 40 meters from pavements except in unusual circumstances such as ditches draining road surfaces.

Profile studies have also been completed and a comparison between a typical urban soil profile and a rural profile is shown in Figure 9. Concentrations shown are averages of 10 profiles. The urban profiles were taken within 10 m of a city street (12,000 vehicles/24 hrs). While the rural profile was taken in an agricultural field remote from a highway. Maximum concentrations are found in the upper 10 cm with a sharp decline in concentration between 10 and 20 cm. Below 20 to 30 cm the lead

## SOIL PROFILE ANALYSIS

	URBAN	RURAL
0-10 CM	390 PPM	16 PPM
10-20 CM	165 PPM	9 PPM
20-30 CM	48 PPM	7 PPM
30-40 CM	40 PPM	6 PPM
40-80 CM	19 PPM	4 PPM

Figure 9. Typical Urban and Rural Soil Profiles



concentration is relatively uniform. Considerably higher concentrations are evident in the urban profiles which again shows a strong correlation to traffic volume.

Intensive studies on lead in the vegetation of the ecosystem were carried out during summers of 1971, 1972, and 1973. The influence of the proximity and direction from highways was similar to that observed for soils. Sampling was completed at the time of full maturity of plants in the field. Along the heaviest travelled roads, there was significantly more lead in/on corn and soybeans within 30 meters of the pavement but by 40 meters from the pavement lead in/on crops was not different from the average for the field. On lesser travelled roads, there was no observable influence of the highway on crop lead. Along the heavily travelled roads, corn and soybeans growing within 30 meters of the pavement averaged about 30 ppm lead whereas plants farther away from the pavement and along secondary roads averaged 8-10 ppm. Analysis of grain from corn and soybeans showed a consistently low lead content averaging less than 2 ppm.

Lead content in the vegetation of the ecosystem is summarized in Table 9. The size (223 Km<sup>2</sup>) and diversity of the watershed precluded a routine approach to sampling.

Summary of Lead Content of Vegetation and Habitat Areas in a Champaign County Watershed.

Habitat	Total Area (Km <sup>2</sup> )	Percent of Av. Pb content Watershed of Vegetation	Average Dry Biomass (gms) of Vegetation/m <sup>2</sup>	Total Pb in Vegetation of compartment (gms)
A. Urban				
1. Pervious	18.986	8.5	150*	156,640*
2. Impervious	12.657	5.7	--	--
B. Rural				
1. Fields				
a. Cultivated	166.383	74.6	1400	1,863,330
b. Sod	3.805	1.7	800	124,804
2. Roads				
a. Class I pavement roadside	0.776	0.3	--	--
b. Class II pavement roadside	1.551	0.7	154	7,643
c. Class III pavement roadside	0.026	<0.1	--	--
d. Class IV pavement roadside	0.051	<0.1	155	166
e. Class V pavement roadside	0.113	<0.1	--	--
f. Class VI pavement roadside	0.226	0.1	194	685
g. Class VII pavement roadside	0.143	<0.1	--	--
h. Class VIII pavement roadside	0.285	0.1	288	740
i. Class IX pavement roadside	1.091	0.5	--	--
j. Class X pavement roadside	2.181	0.9	262	4,286
3. Railroad				
a. Track pavement	0.524	0.2	--	--
b. Right-of-way	0.524	0.2	520	1,825
4. Homestead	5.899	2.7	100*	2,250*
5. Streams	3.120	1.4	623**	9,156
6. Fencerows	3.000*	1.3	691	9,023
7. Waste Areas	2.980	1.3	664**	10,862
8. Woods	1.533	0.7	75**	989
9. Pond (Surface Water)	0.324	0.1	--	--
TOTAL	223.178	(86.147 miles <sup>2</sup> )		

\*Estimate based on preliminary data

\*\*Herb Layer only

Consequently, the watershed was divided into rural and urban compartments. The rural compartment was subdivided into vegetation habitats. A description of the divisions is given below:

A. Urban: All area within the watershed developed for residential or industrial use. (Single dwelling sites, such as farm houses and collected outbuildings were grouped into a rural subcompartment called homesteads.) Roads, railroads, vacant lots, streams, parks and so forth, within the general urban area, were included as urban and not further identified at this time.

1. Pervious: All non-paved surface.
2. Impervious: All paved surface including roofs.

B. Rural

1. Fields

a. Cultivated Fields: All crop fields that were tilled within the last year.

b. Sod Fields: All crop fields and/or pastures that are tillable

2. Roads (see section on traffic sampling)

a. Pavement

b. Roadsides: Up to and including bordering fencerows.

3. Railroads
  - a. Track Pavement
  - b. Right-of-Way: Up to and including fencerows.
4. Homesteads (see Urban description)
5. Streams: All vegetation bordering streams that was not utilized for crops or pasture. In waste areas, this included only the stream bank vegetation.
6. Fencerows: All untilled area between fields whether a fence was present or not.
7. Waste Areas: Miscellaneous areas not identified in other categories. Includes refuse areas, dry borrow pits, permanently fallowed fields which lacked complete arborescent cover, rural cemeteries, and unused areas around isolated outbuildings.
8. Woods: Forested areas with all or nearly all arborescent cover.
9. Ponds: Generally borrow pits. Includes surface water only.

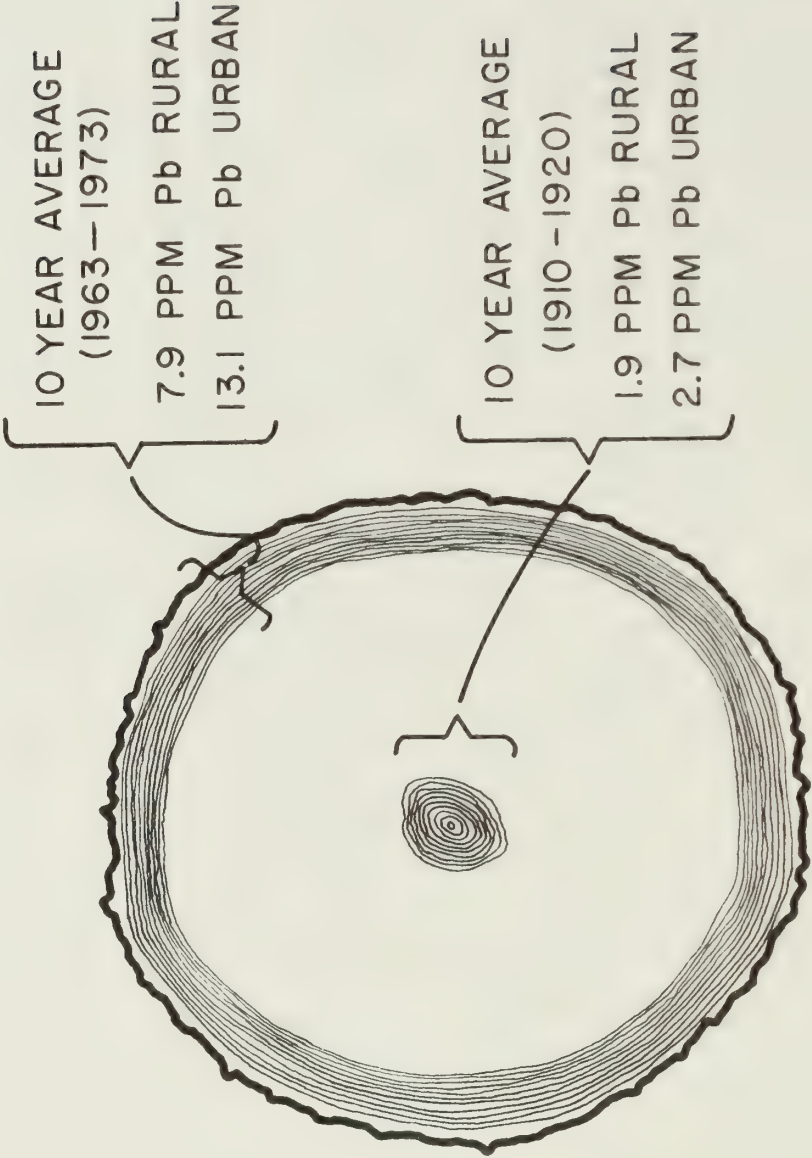
All compartments and subcompartments were sampled, except the urban area (to be completed in 1974), with 1/4 m<sup>2</sup> circular frames randomly located within a defined

compartment. Transects were used to ascertain lead content relative to distance and direction from roads but, with the exceptions noted above for crops, traffic flow had no influence on lead content. Total area for each compartment and subdivision was determined from aerial photographs of the watershed. Ground checks were made in all cases where vegetation or use of an area was unclear. Because sampling was random within each subcompartment, the observed biomass (averaged) was multiplied by total area to arrive at total biomass. All sampling was done at peak standing crop. Average lead content of the vegetation in the subcompartment was then used to calculate total lead for the subcompartment (Table 9).

Temporal distribution of lead is shown in Figure 10 for urban and rural tree ring samples. The urban samples were collected from trees within 10 m of heavily travelled city streets with greater than 10,000 vehicles per 24 hours. The rural samples were collected from trees within 10 m of a country road with an average traffic volume of 1,800 vehicles per 24 hours. Values shown are averages of 20 samples and show a significant increase between 50 year-old tree rings and current rings.



FIGURE 10. TREE RING ANALYSIS OF URBAN AND RURAL TREES.



### References

Cantwell, E. N., E. S. Jacobs, W. G. Cunz, Jr., and V. E. Liberi, 1972 "Control of Particulate Lead Emissions from Automobiles", Cycling and Control of Metals, U.S.E.P.A., Cincinnati, Ohio, pp. 95-107.

#### A. Lead in Small Mammals

Samples of small mammals were obtained by snaptrapping from the following situations: within 10 m of a high-use road ( $>12,000$  vehicles/24 hrs), within 5 m of medium-use roads (2,000-6,000 vehicles/24 hrs), and within 5 m of low-use roads ( $<400$  vehicles/24 hrs). Control samples were taken from situations at least 50 m away from any road (normally the closest road was a low-use road). Trapping was done seasonally (November, March, June, and August) for the last 2-1/2 years.

All specimens were thoroughly washed in glass distilled water to remove as much particulate lead on the fur as possible and then freeze-dried. The entire animal (including digestive tract) was processed when the dried specimen weighed less than 10 grams. Specimens heavier than 10 grams dry weight were ground in a blender and one gram subsamples processed for lead analysis. All lead concentrations were recorded in ppm dry weight.

Results of the studies are shown in Table 10. All species except Peromyscus leucopus had higher lead concentrations in habitats adjacent to the heavy-use road. Since the home range of Peromyscus leucopus averages more than 50 m in diameter, even those individuals caught the closest to the highway undoubtedly were spending a

Table 10

Total lead in entire carcass (including digestive system) of small mammals in relation to the level of traffic on adjacent roads. All specimens except controls were taken within 10 m of road; controls were captured a minimum of 50 m from any road. All data are presented in ppm dry weight; figures in parentheses indicate sample size.

Species	Heavy Traffic	Medium Traffic	Low Traffic	Controls
<u>Blarina brevicauda</u>	15.2(46)	6.5(71)	3.9(49)	3.6(16)
<u>Cryptotis parva</u>	12.3(13)	5.4(3)	3.2(3)	7.4(7)
<u>Microtus ochrogaster</u>	8.2(40)	4.3(60)	2.6(50)	3.3(13)
<u>Spermophilus</u> <u>tridecemlineatus</u>	-	8.2(13)	-	4.3(17)
<u>Peromyscus leucopus</u>	2.5(16)	2.6(23)	-	2.7(4)
<u>Peromyscus manicu-</u> <u>latus</u>	5.5(57)	3.7(103)	2.6(63)	2.8(99)
<u>Reithrodontomys</u> <u>megalotis</u>	10.8(32)	3.8(23)	3.1(6)	3.1(20)
<u>Mus musculus</u>	6.9(51)	3.5(150)	4.2(59)	4.6(104)

considerable amount of time much further removed. This probably accounts for the low level of lead in this species.

Lead concentrations in small mammals taken along medium-use roads were only slightly higher, if at all, than in those from along low-use roads. There was no significant difference in lead concentrations in small mammals taken along low-use roads and those taken more than 50 m away from any road.

Along heavy-use roads there was a correlation between habitat requirements and lead concentrations in small mammals. Species which require dense vegetation and which do not occur out in cultivated fields (Microtus ochrogaster, Blarina brevicauda, Cryptotis parva, and Reithrodontomys megalotis) had higher lead concentrations than did those species that also extend their home ranges out into cultivated fields, and thus more than 50 m from roads (Peromyscus maniculatus and Mus musculus).

There was no correlation between lead concentration in the small mammals and the season of the year.

Along heavy-use roads there was a general correlation between feeding habits and lead concentration in the body tissues. Insectivores (Blarina and Cryptotis) had highest concentrations of lead; herbivores (Microtus ochrogaster)



had intermediate levels; granivores (Peromyscus maniculatus, Peromyscus leucopus, and Mus musculus) had the lowest levels of lead recorded. Reithrodontomys megalotis (a granivore) did not fit this pattern; likewise, Spermophilus tridecemlineatus (also a granivore) showed higher levels of lead than other species along medium-use roads. The reasons for the differences in these two species could not be determined; the small sample size may be at least partially responsible in regard to Spermophilus.

The higher lead concentration in Blarina and Cryptotis may result from food chain concentration. Insects taken from areas adjacent to high-use roads also show relatively high concentrations of lead. Carnivorous insects in these sites display higher lead concentrations than do herbivorous or granivorous species. The shrews may also be concentrating lead from the insects on which they are feeding.

Total body lead burdens appear, in general, to be relatively low in all species of small mammals studied. There is no information as to any possible influence of lead concentrations of this order of magnitude on the various population parameters. Even if the lead has a deleterious effect, however, it would not be a significant factor in the maintenance of populations of the species

studied. Habitats within 50 m of heavy-use roads constitute 12.5% of the total available habitat for Microtus ochrogaster, Reithrodontomys megalotis, and Cryptotis parva; only 11% of available habitat for Blarina brevicauda; less than 1.5% of available habitat for Peromyscus maniculatus and Mus musculus; approximately 10% of available habitat for Spermophilus tridecemlineatus; and less than 1% of the total available habitat for Peromyscus leucopus. Any increased mortality or reduced reproduction resulting from the lead taken up by the small mammals would affect only a minor segment of the total population of any species in the study region. Such losses would quickly be replaced by dispersal from adjacent populations.

Estimates of the total amount of lead in residency at any given time in the small mammals in the rural compartment of the total ecosystem are as follows:

If all species were at maximum density at the same

time: 47.2 g

If all species were at lowest density at the same

time: 2.2 g

Best estimate of average amount of lead in residency

at any given time: 23.7 g

There is thus a very small amount of lead in residency in the total standing biomass of small mammals in the

ecosystem study area at any given time.

Tissue lead distribution studies are currently underway. Preliminary data are shown in Table 11 and indicate higher concentrations in the bone and digestive tract as would be expected. Since sample sizes are small and the variance is high conclusions from these preliminary data are not warranted. Approximately 1,000 samples have now been processed for analysis to obtain statistically significant data.

Major efforts during the 1973 study were directed at (1) obtaining sufficient samples of small mammals for tissue analysis; (2) collecting birds from the urban and rural compartments; (3) obtaining selected specimens of larger mammals from the urban and rural compartments, and (4) collecting representative amphibians and reptiles from these compartments.

#### Large Mammals

Comparisons are being made of the lead content of selected organs of large mammals from urban and rural compartments (primarily away from roads in the latter compartment). Specimens from the urban compartment are most representative of animals from areas of high lead since these animals can be assumed to have spent

Table 11

Preliminary analyses of lead content (ppm dry wt) of selected tissues and organs from small mammals taken within the high lead zone along an interstate.

<u>Species</u>	<u>Intestinal</u>	<u>Spleen</u>	<u>Liver</u>	<u>Lung</u>	<u>Femur</u>	<u>Thigh</u>
Bb(19)*	31.2	8.0	6.0	15.5	74.0	16.7
Pm(11)	22.3	18.0	4.2	8.3	19.5	9.4
Mo(4)	10.6	15.0	2.0	5.2	19.2	12.4
Mn(6)	21.5	88.5	5.6	14.2	63.2	14.8

\*Sample size in parentheses.

Bb = Blarina brevicauda

Pm = Peromyscus maniculatus

Mo = Microtus ochrogaster

Mn = Mus musculus

most, if not all, of their lives in areas of high lead. Individuals taken on high-use highways in the rural compartment probably have not spent much time in the high-lead zone adjacent to the road. Most species of larger mammals do not feed along the roads; their home ranges are sufficiently large that little time would be spent in the vicinity of the highway, even though they were killed on the highway. Results are presently incomplete.

#### Birds

The following species are being examined to compare lead content of individuals in the urban and rural compartments: robin, grackle, starling, house sparrow, and pigeon. As in the case of the large mammals, individuals living in the urban compartment are probably most representative of animals from high lead areas. A total of 126 specimens have been collected to date.

Individuals of species that nest in grassy areas along interstate will also be compared with specimens of same species living away from the interstate. To date specimens of the red-winged blackbird have been collected. During the spring of 1974 additional specimens will be collected. Young from the nest will be used since they are easier to obtain and will reflect more clearly the differences in environmental lead levels.



## B. Lead in Insects

Insects were sampled during the 1973 growing season at sites listed in Table 12. Lead analysis and estimation of biomass are in progress. The number of samples completed and the total number taken are also given in Table 12. All samples were washed in distilled water, dried and weighed before being sent for lead analysis. New lead analysis techniques permitted use of only 10 mg samples of insects, which accounts for the larger number of samples than in 1972, and which permitted more detailed analysis of lead content in specific insect groups.

The most abundant insect groups and lead contents and biomass are given in Table 13. There were no consistent seasonal trends in lead content of insects so samples have been grouped. Insects are listed according to their feeding type: sucking insects suck plant juices; chewing insects chew up the whole leaf; the predators eat other insects. The families listed are Cicadellidae (leaf hoppers), Miridae (plant bugs), Tettigoniidae (long-horned grasshoppers), Acrididae (short-horned grasshoppers), Syrphidae (flower flies - in larval stage they are predators of aphids), Formicidae (ants - predators and scavengers). Urban sample sites are grouped into Class I

Table 12. Number of samples taken and number analyzed for insect studies of lead in an ecosystem, 1973

Sites	No. of lead analysis samples	No. of lead analysis samples returned	Number of biomass samples	Number of biomass samples analyzed
Urban				
I-74 N. Close	41	40	15	5
I-74 N. Far	37	35	15	5
I-74 S. Close	89	67	20	2
I-74 S. Far	115	86	20	0
Green St.	50	50	20	10
Florida Ave.	34	28	25	6
Class III	36	33	25	3
Class V	18	18	20	6
Rural				
I-74 N. Close	97	49	15	7
I-74 N. Far	126	110	15	5
I-74 S. Close	161	117	25	12
I-74 S. Far	234	206	25	16
Brownfield Meadow	142	139	30	9
Brownfield Woods	15	14	15	8
Phillips Tract	111	104	25	12
Totals	1306	1096	310	106

Table 1.3. Lead content of insects in Urban and Rural compartments of ecosystem

Sample site	Sucking Insects			Chewing Insects			Predators			Total Biomass										
	(Cicadellidae) Leaf-Hoppers	(Miridae) Plant Bugs	(Tettigoniidae) Long-Horned Grasshoppers	(Acrididae) Short-Horned Grasshoppers	(Syrphidae) Flower Flies	(Formicidae) Ants-Predators and Scavengers														
	No. samples	Mean $\pm$ S.E.	Range	No. samples	Mean $\pm$ S.E.	Range	No. samples	Mean $\pm$ S.E.	Range	No. samples	Mean $\pm$ S.E.	Range	No. samples	Mean $\pm$ S.E.	Range	No. samples	Mean $\pm$ S.E.	Range		
Urban Class I	78	15.0 $\pm$ 2.7	2-110	6	29.5 $\pm$ 5.4	22-83	28	63.2 $\pm$ 5.1	21-140	2	57.5 $\pm$ 26.5	31-84	22	39.6 $\pm$ 8.0	13-190	19	99.1 $\pm$ 14.6	3-240	7	189.6 $\pm$ 60.3
Class III	0			3	6.2 $\pm$ 2.9	2-12	5	77.4 $\pm$ 16.0	17-110	0			10	24.9 $\pm$ 11.1	4-100	12	54.6 $\pm$ 16.9	17-220	3	33.2 $\pm$ 17.0
Class V	5	5.74 $\pm$ 4.1	1-22	0			0			0			6	6.7 $\pm$ 1.1	3-11	6	66.8 $\pm$ 21.5	16-130	6	92.4 $\pm$ 3.5
Rural I-74	42	11.6 $\pm$ 3.5	1-150	8	11.0 $\pm$ 2.8	5-29	39	49.4 $\pm$ 3.5	11-120	28	13.4 $\pm$ 1.1	2-22	19	12.9 $\pm$ 1.2	5-24	27	52.3 $\pm$ 7.7	4-120	16	196.5 $\pm$ 36.2
Brownfield	44	10.5 $\pm$ 1.8	2-66	9	7.5 $\pm$ 2.6	3-28	4	44.5 $\pm$ 13.0	9-71	4	10.8 $\pm$ 1.9	6-15	17	15.8 $\pm$ 2.8	5-40	33	21.5 $\pm$ 1.4	8-44	9	75.0 $\pm$ 23.6
Phillips	21	7.8 $\pm$ 1.8	1-27	17	5.4 $\pm$ 0.8	2-12	1	4.8		0			4	5.5 $\pm$ 2.0	3-11	5	10.4 $\pm$ 2.4	5-18	11	141.4 $\pm$ 22.2

roads with an average daily traffic (ADT) of over 10,000, Class III roads (ADT 2500-4999) and Class V roads (ADT less than 1000). The low biomass of insects in Class III and V areas, and the small areas available for sampling, resulted in small sample sizes. Malaise traps will be used in 1974 to increase sampling efficiency.

Sampling in rural areas was restricted to Interstate 74, (ADT = 13,000), Brownfield meadow (ADT = 575) and the Phillips tract which was remote from a paved road and provided data on base line levels of lead in insects. Brownfield Woods was sampled but insect abundance was very low in 1973 as estimated by the D-Vac sampler. Malaise traps should provide larger sample sizes.

The data support the conclusions reached in the 1972 sampling. Sucking insects contained less lead on average than chewing insects, and these herbivores had lower levels than mean lead content of predators. Also lead content in insects is correlated with the lead emission levels from automobiles. However when these groups are broken down as in Table 13 considerable differences in lead content are apparent even between families of the same feeding type. Even within a type and sample site lead levels are highly variable as indicated by the range column.

New findings derived from the 1973 data are that levels of lead in insects in the urban compartment are considerably higher in the Class I areas than in the rural compartment: the chewing insects have much higher lead levels than estimated in the 1972 data: ants have massive doses of lead relative to other terrestrial insects. Only two samples of ants were taken in 1972 and both were abnormally high. The 1973 data again suggest that ants have unusually high levels of lead, although the levels are exceedingly variable within a particular site. Since ants forage extensively on the ground, and prey on a diverse array of insects and dead material, they probably receive high levels of lead both topically and orally.



### C. Lead in the Aquatic System

#### Sediment

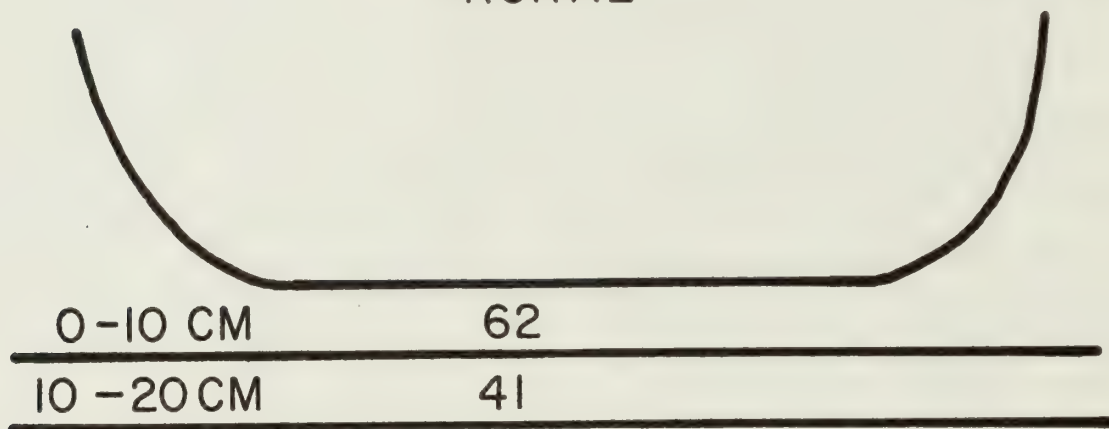
The distribution of lead in aquatic sediments to a depth of 30 cm is shown in Figure 11 for sediments from the urban and rural subcompartments. Profile concentrations shown are averages of 10 profiles in each subcompartment. Very high concentrations are found in the urban subcompartment due to the large quantity of particulates washed from urban impervious surfaces into the Boneyard Creek. The high sediment concentrations indicate possible danger to urban aquatic food chains.

#### Biota

Lead distribution was derived by measuring the populations of major plant and animal taxa and their lead contents. Only the drifting invertebrates constitute a measurable transport of lead through the ecosystem by aquatic organisms. The amount of drift has been measured. Arriving at exchange rates between trophic levels is the most difficult assignment. Lead levels of individual organisms, experimental investigations of lead uptake and loss, and reviews of the biology of certain taxa have been employed to indicate the dynamics of individual accumulation mechanisms.

## STREAM SEDIMENT ANALYSIS

## RURAL



## URBAN

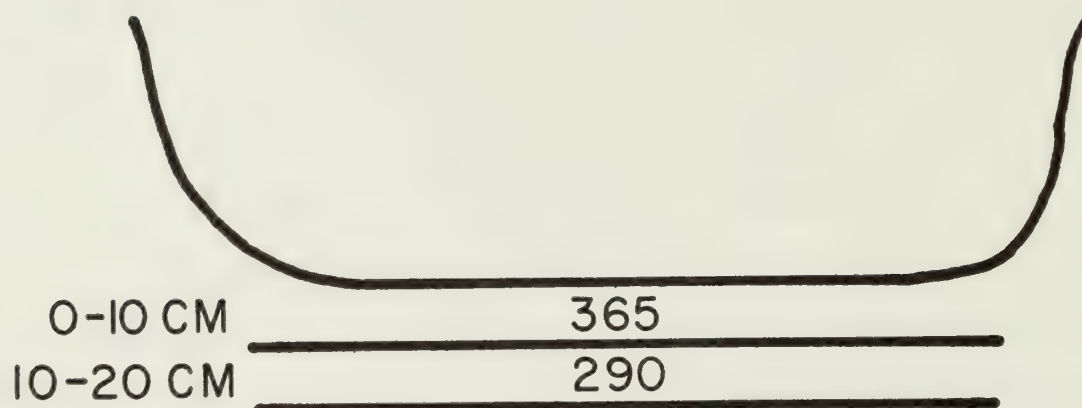
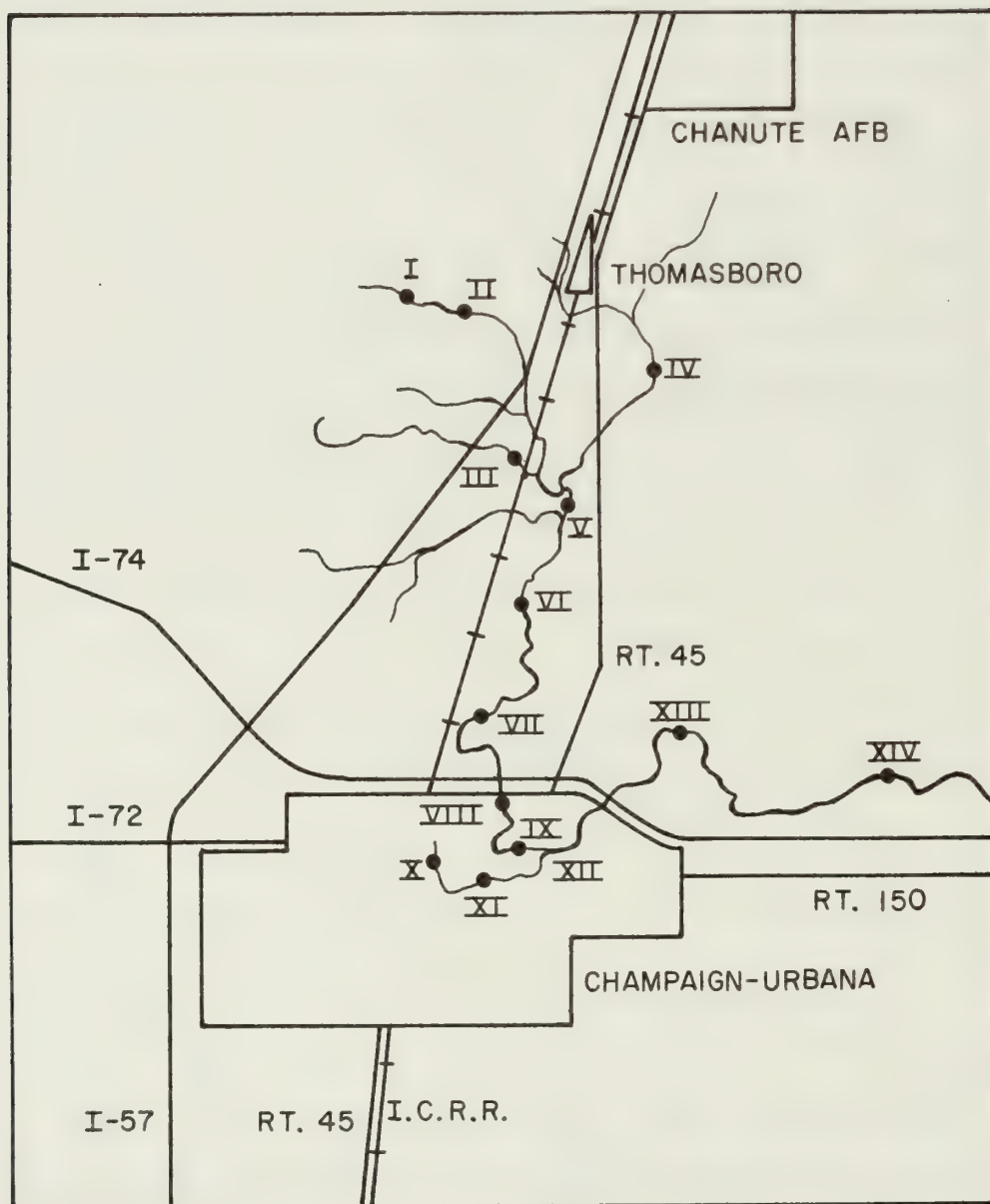


Figure 11. Lead in Stream Bottom Sediments for Urban and Rural Compartments

The study area is the entire drainage of the Saline Ditch above Mayview, Illinois. About two-thirds of the 40 miles of stream is channelized, rural flow. The major sources of lead--the city runoff, high-use roads, and waste treatment facilities--are concentrated in the urban area. Sampling stations in five study area divisions have been designated (Figure 12). The Rural Compartment contains a few high-use roads and a subdivision (the Rural Sub-compartment) which has no major lead sources. The Urban Compartment is Boneyard Creek which consists only of runoff from Champaign and Urbana. The Marginal Compartment is a transition zone for the rural flow entering the urban environs. The sum of the flows from the Rural and Urban Compartments and the Urbana waste treatment plant forms the Combined Compartment.

Filamentous algae (Cladophora, Spirogyra) occurs periodically throughout the entire study area. Elodea which was found in great quantity in 1972, in the Combined Compartment, occurred in only scattered patches in 1973. Similarly, Potamogeton was found in great quantity in 1972, in the Rural Compartment, but none was found in 1973. Semiaquatic plants were found in the Rural Sub-compartment and Marginal Compartment after prolonged low water.



RURAL SUBCOMPARTMENT - I+II  
 RURAL COMPARTMENT - I-VII  
 MARGINAL COMPARTMENT - VIII+IX  
 URBAN COMPARTMENT - X-XII  
 COMBINED COMPARTMENT - XIII+XIV

Figure 12. Aquatic Studies Sampling Locations

Sampling patches of rooted plants is easily accomplished by removing plants from a  $1/4 \text{ m}^2$  sampling device. Accurate quantitative sampling of algae is difficult because of its growth habits. Collecting techniques are being devised to overcome this problem.

Considering the drainage system as a whole, the filamentous algae were the dominant aquatic plants in 1973, while in 1972, the vascular plants dominated. Preliminary studies show a clear pattern of lead levels emerging, but no accurate biomass data are yet available on algae. Observations indicate that the aquatic plants in the Saline Ditch represent a large and highly variable biomass. Aquatic plants seem to accurately reflect relative lead levels. Collections made on the same day, from the Boneyard stations (X, XI, and XII) show a marked reduction in lead levels from the center of the urban area to the edge (Table 14, Figure 12). This is a short distance geographically, yet the plant lead levels accurately reveal this lead gradient. The urban plant lead levels are about 34 times as high as rural plants and the combined area plants are about 4 times as high.

Quantitative sampling is carried out in two-month periods corresponding to the general seasons. Efficient



Table 14

Lead levels (ppm) of aquatic plants in the Saline Branch during the summer of 1973.

<u>Station</u>	<u>Plant Type</u>	<u>Mean Lead Level</u>	
I	Semiaquatic plants	9.5	
I	Fil. Algae	16	Rural Comp.
II	Fil. Algae	8.8	10.2
II	Semiaquatic plants	8.6	
III	Fil. Algae	9.8	
<hr/>			
X	Fil. Algae	515	
XI	Fil. Algae	315	Urban Comp.
XII	Fil. Algae	210	346.7
<hr/>			
XIII/XIV	Fil. Algae	34.9	Comb. Comp.
XIII/XIV	<u>Elodea</u>	42.8	38.2

fish sampling by isolating portions of stream with two seines and removing the trapped fish is possible due to the uniform nature of the channelized bed. Benthic samples are taken with a 1/300 m<sup>2</sup> piston coring device in areas of high population density and a 1/25 m<sup>2</sup> Larimore grab sampler in areas of lesser abundance.

Every third month is spent in sample preparation and data compilation. Organisms are identified, wet weighed, dried, and ground to a homogeneous powder. Fish and plants are dried directly from water. Benthic organisms are stored in 95% ETOH to facilitate handling and drying. Analyses are performed at the laboratory facility.

Since benthic samples are taken according to substrate type, an accurate survey of the stream was necessary. In June, 1972, 130 stations on 25 miles of stream were examined to determine average width and depth, proportions of bottom types, and occurrence of aquatic plants. This survey is modified by spot-check each season.

The amount of lead associated with the biota in the various compartments is irregular with respect to time and location. The differences reflect both variation in biomass and lead levels (ppm) of the organisms.

The Rural Compartment has a diverse, changeable population. Representatives of 15 orders of invertebrates and 17 species of fish were collected in the first year of work. The benthic biomass varies seasonally due to hibernation of crayfish, emergence of insects, and elimination of organisms by adverse conditions (Table 15). The concentration of lead in the rural biota does not change measurably with time (Table 16). Fluctuations in the fish population are slight. Changes in lead density follow population growth (Figure 13).

There are only four families of invertebrates present in significant quantities in Boneyard Creek (the Urban Compartment). None of the species is seasonal and fluctuations in the biomass density are small. The major shift in lead accumulation occurs due to changes in the lead levels in the organisms. These changes are apparent in particular taxa (Table 16) and in the entire population (Figure 13).

The Combined Compartment is directly affected by the sewage treatment plant. The biomass consists of several pollution-tolerant benthic organisms, some aquatic plants, Elodea sp. and Cladophora sp. Fluctuations occur in a much shorter time period (Figure 14). Lead levels do not vary seasonally in the benthic organisms

Table 15  
Seasonal Biomass Density of the Fish and Benthos  
in the Saline Ditch

<u>Compartment</u>	<u>Spring</u>	Density of Biota ( $\text{g/m}^2$ )				
		1972	<u>Fall</u>	<u>Winter</u>	1973	<u>Summer</u>
		<u>Summer</u>			<u>Spring</u>	
Rural Sub-	10.6	3.8	3.0	6.3	4.6	1.3
Rural	2.5	3.0	2.8	5.0	4.5	1.2
Urban		3.7	3.0	10.5	2.8	1.0
Combined		11.4	18.5	109.2	5.9	3.0

Table 16  
Lead Levels (ppm) of Representative Organisms in  
the Major Areas of Interest During 1972

	Spring	Summer	Fall	Winter
Rural Area-----				
Tubificidae		17	14	14
Chironomidae		11	24	9
<u>Physa</u> sp.		11		
Urban Area-----				
Tubificidae	125	119	363	484
Chironomidae		111	340	260
<u>Physa</u> sp.				38
Combined Area-----				
Tubificidae	36	45	46	43
Chironomidae	46	45	51	
<u>Physa</u> sp.		55	48	



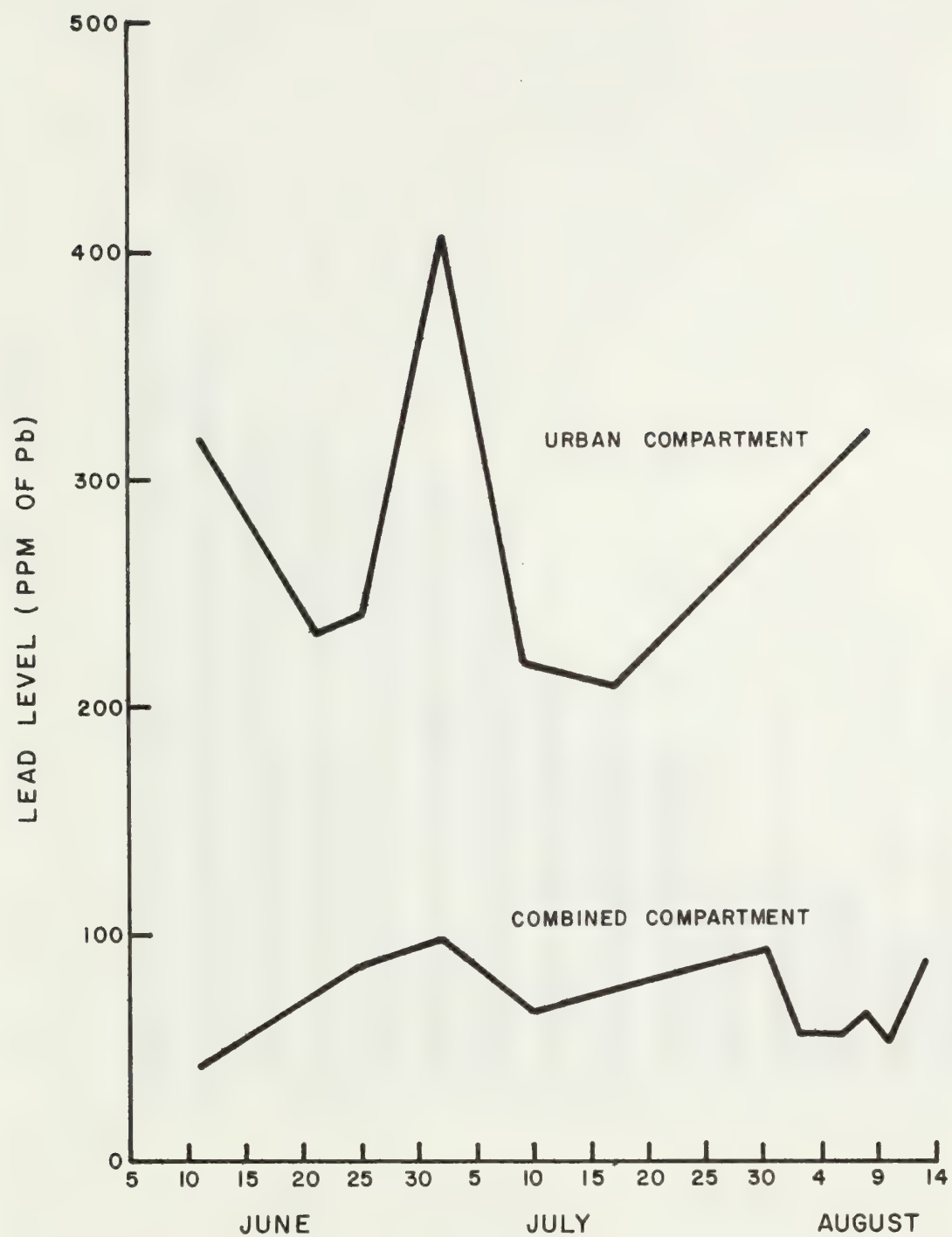


Figure 13. Population Growth and Lead Density

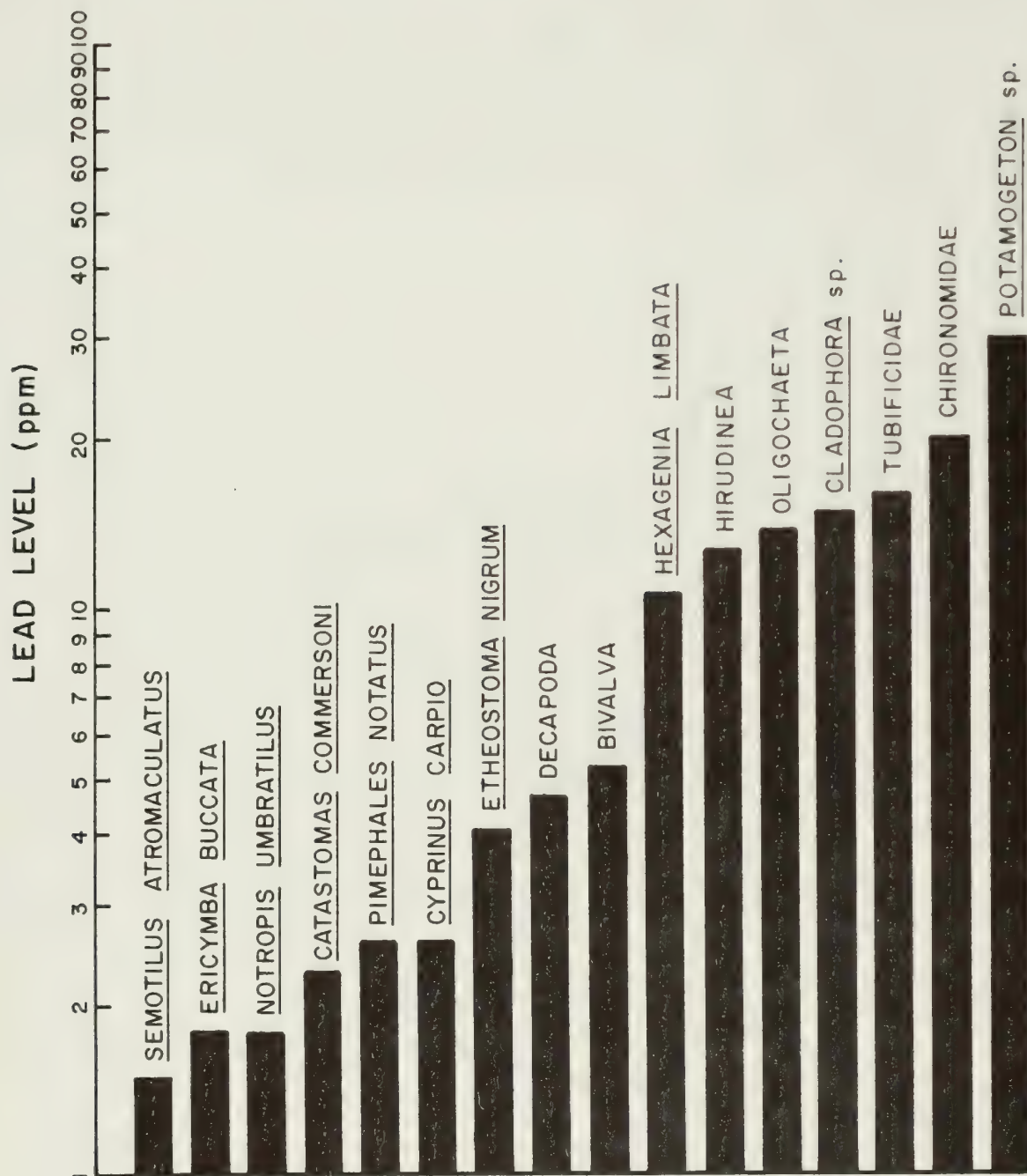


Figure 14. Lead Level (ppm) in Aquatic Organisms

(Table 16). Shifts in population density occur where the oxygen level increases in colder weather.

The macrophytes and fish do not make measurable contributions to the loss of lead from the areas except perhaps as suspended solids in the water mass. The efflux of benthic organisms from a compartment may occur through emerging insects and drifting invertebrates. Predicting the amount of emerging insects in an area is, at best, difficult and has not been accomplished. The Pb levels in adult chironomids are comparable with levels of immatures. The lead lost in drift from the Rural and Urban Compartments is insignificant when compared with the amount lost in the water and suspended solids (Table 17).

The findings of this study concur with those of Mathis and Cummings 2 in their 1972 Water Resources Center Research Report, "Distribution of Selected Metals in Bottom Sediments, Water Clams, Tubificid Annelids, and Fishes of the Middle Illinois River." Lead does not concentrate in higher trophic levels of aquatic food webs (Figure 17). The lead levels in organisms are more closely associated with their micro-habitat than their trophic position. In the rural area Etheostoma nigrum has much more lead than Semotilus atromaculatus (Table 18)

Table 17

Lead flow associated with the biota, water, and suspended solids originating in the Rural and Urban Compartments during periods of peak invertebrate drift.

Compartment of Flow Origin	mg of Lead per 100 m <sup>3</sup> of Water in August			
	Filtered Water*	Suspended Solids*	Stream Drift 1972	Stream Drift 1973
Rural	163	622	0.0016	0.0004
Urban	171	5020	0.0005	0.23
Combined	169	3941	0.0004	0.0019

\*Filtered water and suspended solids data from Progress Report of October, 1972.

Table 18

Approximate Lead Levels (ppm) of Representative Organisms  
from the Aquatic Ecosystem

<u>Organisms</u>	<u>Compartments</u>					
	<u>Rural</u>	<u>Sub</u>	<u>Rural</u>	<u>Urban</u>	<u>Marg.</u>	<u>Comb.</u>
Hirudinea		17	13			
Oligochaeta		17	13	48		
Tubificidae		11	16	368	38	49
Bivalva			5			
Physa sp.		12	12	38		42
<u>Lirceus fontinalis</u>		8	8			
<u>Hexagenia limbata</u>		5	10			
Chironomidae		15	20	153		43
Anisoptera		7	7			
Decapoda		2	5	11		
<u>Cladophora</u> sp.		12	15	347		35
<u>Potamogeton</u> sp.		15	30			
<u>Elodea</u> sp.						90
<u>Etheostoma nigrum</u>			4.1			
<u>Cyprinus carpio</u>		2.5	2.6			
<u>Pimephales notatus</u>		2.6	2.6			
<u>Catastomas commersoni</u>		2.0	2.3			
<u>Ericymba buccata</u>		1.8	1.8			
<u>Notropis umbratilis</u>		2.7	1.8			
<u>Semotilus atromaculatus</u>		2.0	1.5			



although they are both predator fish. E. nigrum lives entirely on the bottom while S. atromaculatus lives in levels of between organisms in the rural and urban environs. The most significant differences in these environments exist in the amount of lead in the sediments and suspended materials.

The amount of lead in the biota of any section of stream is a function of both biomass and lead concentration. In rural areas the biomass fluctuation is the controlling factor. The variable lead accumulation in the biota of urban areas overshadows the population changes. The loss of biologically associated lead from any area of stream is insignificant except as suspended material. Lead accumulation in the biota is a complex interaction. The final concentration in all organisms is apparently influenced by the immediate environment.

### Conclusions

Major lead pools of the ecosystem occur in soils, stream bottom sediments and plants (Table 19). In terms of magnitude, other lead pools are negligible. However, consideration should be given to these pools as their importance to the biota could be considerable. Lead in the small mammal, insect or aquatic species may eventually result in serious effects on these components. However,

Table 19

Preliminary Estimates of Ecosystem Lead Pools in Kilograms

<u>Component</u>	<u>Magnitude (kg)</u>
Soil	$9 \times 10^5$
Plant	$4 \times 10^3$
Mammal and Insect	<20 kg
Stream Sediments	$3 \times 10^3$
Aquatic Biota	<20 kg

current evidence does not support this hypothesis. Food chain magnification in the insect compartment and consumption of these insects by organisms at upper trophic levels such as insectivorous birds is likewise a potential problem area and is currently under study.

Considering the larger pools, ecosystem trouble spots include soil plant zones along major highways and in urban areas and the stream sediment biotic interface in the urban area.

## III. S-W-A-P

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### III. SWAP

#### A. Atmospheric Lead - Automobile Exhaust Particulates Background

The results of numerous studies of the particulate matter in automobile exhaust have been reviewed in Habibi, 1973 or otherwise reported in McKee and McMahon, 1960; Ter Haar and Bayard, 1971; Lee et al., 1971; Moran et al., 1971; Moran et al., 1972; Robbins and Snitz, 1972; Sampson and Springer, 1973; Smythe, 1973. Most of these previous studies have been concerned with the content and composition of lead compounds, because of their toxic nature, or with particle size distribution, because of the effect of particle size on the degree of inhalation and retention by the lungs, on reduction of visibility in the atmosphere, and on particle-particle or particle-gas interactions.

In studies with leaded gasoline being burned x-ray diffraction was used to show that lead bromochloride,  $\text{PbBrCl}$ , is the most abundant lead containing compound in exhaust particulates, with lesser amounts of the alpha and beta forms of the double salt ammonium chloride lead bromochloride,  $\text{NH}_4\text{Cl} \cdot 2\text{PbBrCl}$ , Hirschler et al., 1957 and 1964; and Habibi et al., 1970. One controversial aspect of automobile exhaust particulates from leaded gasoline



has to do with whether the particulates readily lose halogen or not. Pierrard, 1969 found that chemically pure  $\text{PbBrCl}$  is decomposed by ultraviolet light, releasing free bromine and chlorine. Robbins and Snitz, 1972 reported that freshly exhausted particulates readily lose halogen, particularly bromine (up to 70% in the first 20 minutes after being exhausted), even in the absence of sunlight. Ter Haar and Bayard, 1971 also reported a large decrease in the bromine to lead ratio in exhaust particulates within the first hour after being exhausted into a large black bag to exclude sunlight. Moran et al., 1971 and 1972 did not report any change in exhaust particulate composition with time, but did report a significant portion of unidentified bromine and chlorine rich forms of  $\text{PbBrCl}$ . Analysis for bromine to lead ratios in atmospheric particulates, Payne and Lindgren, 1972; Bowman et al., 1972 and in lake sediments, Shimp et al, 1970, indicate little loss of bromine, if it is assumed that  $\text{PbBrCl}$  in automobile exhaust particulates is the major source of bromine and lead coexisting in these samples. Thus, the question arises as to whether the changes in composition that have been reported are due to fundamental properties of the lead compounds themselves, are due to their formation in and interaction with the

remainder of the automobile exhaust, or are due to reactions in the atmosphere.

Very little attention has been given to the organic matter associated with exhaust particulates, or to possible interactions between inorganic and organic phases present. McKee and McMahon, 1960, determined the total olefin content, total carbonyl content and free acidity of the benzene extract of exhaust particulates. Moran et al., 1972 introduced particulate samples without any preliminary separation directly into a high resolution mass spectrometer via a heated probe inlet system. By recording high resolution mass spectra of the volatilized material as a function of increasing probe temperature, Moran determined that aliphatics and aliphatic substituted single ring aromatics constituted 99% by volume of the total volatile organic matter associated with the particulates. Smythe, 1973, conducted a comprehensive analysis of the complex mixture of organic compounds associated with exhaust, but was primarily concerned with particulates from a diesel engine, rather than a spark ignition gasoline engine. Smythe identified approximately sixty individual compounds in diesel exhaust particulates and reported that greater than 99% of the extracted material was saturated hydro-

carbons. Due to the separation scheme used by Smythe, however, most of the more polar oxygenated compounds would have been retained on the alumina columns used for preliminary separation of the particulate extract. Moreover, he did not use a quantitative particle collection system.

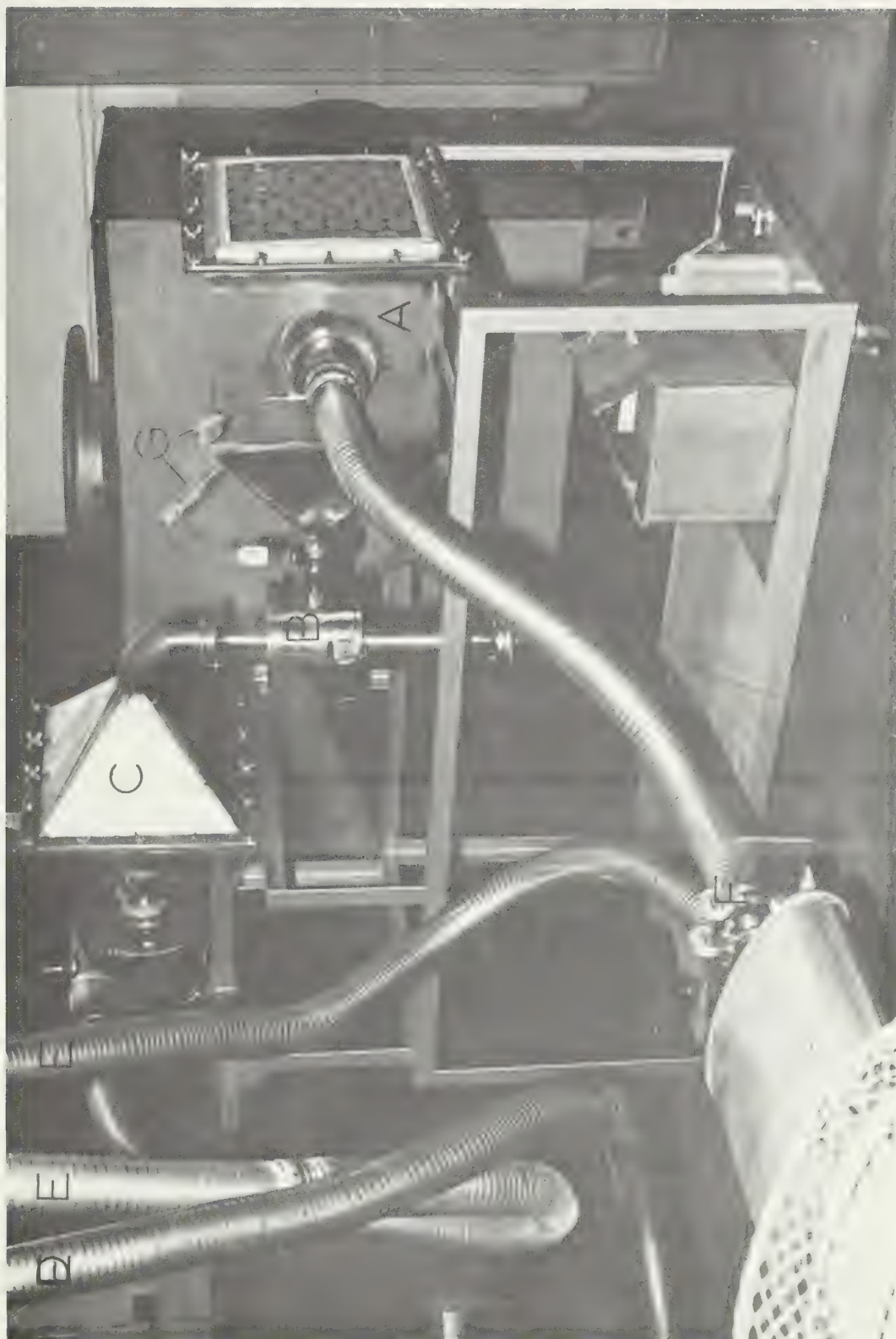
#### B. Experimental

This study was conducted in two parts. First, lead halide aerosols were generated and exposed to various atmospheric conditions to see if changes in the aerosol composition would occur. The results of the lead halide experiments have been previously reported (PR1, pages 138-167 and PR2, pages 41-62). Then, actual automobile exhaust particulates were quantitatively collected and analyzed.

Using the particulate collection apparatus shown in Figure 15, automobile exhaust particulates were collected from a 1973 Ford 351 cubic inch V-8 engine coupled to a General Electric Model 1G315 inductor dynamometer. As part of this study, catalytic converters supplied by Universal Oil Products Company were tested for their effectiveness in reducing exhaust particulate emissions. To preclude poisoning of the catalytic converters with lead, a new engine, which had never been run on leaded

Figure 15  
Particulate Collection Apparatus

- (A) Air Mixing Chamber
- (B) Cyclone Separator, Universal Oil Products, Air Correction Division, Sanitary Cyclone, Size 2.
- (C) Filter Chamber Housing 12"x12" Reeve-Angel 934 AH Glass Fiber Filter
- (D) Bendix Model 16003 High Volume Hurricane Air Sampler Blower
- (E) Exhaust Dump Line to Outside
- (F) Two-Way Exhaust Valve
- (G) Temperature Monitoring Thermocouples





gasoline, was obtained. All tests with non-leaded gasoline. For non-leaded tests, the fuel used was lead-free Indolene, a standard full boiling range test gasoline used for exhaust emission studies. For the leaded gasoline tests, the same Indolene was used, with the exception that standard tetraethyl lead motor mix had been added in an amount sufficient to give 2.5 gm Pb/gal of gasoline.

The particulate collection apparatus (Figure 15), which has been described in Boyer, 1974, consisted of four major components: (A) an air mixing chamber; (B) a Universal Oil Products size 2 sanitary (take apart design) cyclone separator; (C) a filter chamber; and (D) a Bendix Model 16003 high volume Hurricane Air Sampler blower. The particulate collection system, which sampled one-half of the total exhaust, provided for dilution and mixing of the engine exhaust with prefiltered air before collection of particulates and for gross size separation of particulates with a cyclone separator during sample collection. This collection apparatus is more sophisticated than that used in Ter Haar et al., 1972, which did not allow for air dilution of the exhaust, but is less complicated than the long tunnel setups in Habibi et al., 1970; Moran et al., 1971, which allow for isokinetic sampling of the air-diluted exhaust stream.

Unless otherwise stated, all samples analyzed were obtained with the engine running at 30 miles per hour cruise. During engine operation, carbon dioxide, carbon monoxide, gaseous hydrocarbons, oxides of nitrogen, and oxygen were monitored to ensure the experimental conditions did not change significantly during a particulate collection run or from one run to the next.

Exhaust particulates were separated into two fractions by the cyclone separator: a fraction of particles larger than a few micrometers in diameter collected by the cyclone separator itself, and a fraction of particles smaller than one or two micrometers in diameter collected on Reeve Angel 934 AH glass fiber filters in the filter chamber. The fraction of larger particles was physically characterized by SEM. The inorganic elements present in the larger particulates were determined by energy dispersive x-ray analysis with an ORTEC lithium drifted silicon x-ray detector Model 78616-04165 (0.3 mil Be window, 165ev resolution) and an ORTEC Model 6200 multichannel analyzer (1024 channels, 200 eV per channel), while the sample was being irradiated with a 30 KeV electron beam in the JSM-U3 SEM. The fraction of smaller particles was similarly characterized with the SEM. In addition, however, the organic phase of the smaller particles was analyzed.

After collection of exhaust particulates, a 12"x12" filter (pre-extracted with ether prior to sample collection) containing the submicrometer particulates was extracted with 200 ml of freshly distilled diethyl ether. The ether extract was concentrated to less than 500  $\mu$ l and a gas chromatogram (GC) obtained under standardized conditions for the concentrated extract. Liquid column chromatography (LC) was used to fractionate the concentrated extract prior to analysis of the fractions by gas chromatography-mass spectroscopy (GCMS).

LC fractionation of the concentrated extract was carried out on 10 cm long x 1 cm diameter activated silica gel columns by eluting with solvent combinations of increasing polarity, Rosen and Middleton, 1955. Fraction a, eluted by pentane, was collected until the eluent began to absorb in the 200-600 nm range. Fraction b, also eluted by pentane, was collected until the appearance of UV fluorescent eluent with the column exit being illuminated in the dark by a hand held Black-Lite UVL-21 ultraviolet lamp. Fraction c, also pentane eluted, was collected until the UV fluorescence changed from strong light blue to strong light green. Fraction d, eluted by 50% pentane/50% ether, was collected until

continued elution did not produce any more fluorescent eluent. Likewise, fraction e was eluted with 50% ether/50% acetone, and fraction f was eluted with 50% acetone/50% methanol. The fractions were concentrated by vacuum distillation to about one ml and then further concentrated to less than 100  $\mu$ l by vacuum evaporation of the solvent in a stream of dried filtered air.

Prior to GCMS analysis the concentrated fractions were analyzed by an off-line GC using the experimental parameters in Table 20. The GC response and retention times were checked daily with a standard mixture of aliphatic and polynuclear aromatic hydrocarbons. A number of GC liquid phases, including SE-30, SE-52, OV-1, OV-17, apiezon L, Carbowax 20 M, and Dexil 300, were tried for GCMS analysis of the fractions. Dexil 300 proved to be the most satisfactory liquid phase, mainly because of the low bleed at the highest end-of-program (eop) temperature (320°C), combined with the excellent separation ability for complex mixtures over a wide temperature range (40°C to 320°C).

Mass spectra were obtained by cyclic scanning mass spectroscopy of the GC effluent with the mass spectra being stored on magnetic tape during the GC run. Data

Table 20  
GCMS Experimental Conditions

Off-line GC:	Varian 1400 GC	Varian 1800 GC
GCMS System:	<u>Mat-111 GCMS System</u>	<u>Varian 2700 GC, CH-7 MS</u>
<u>Parameter</u>		
GC Column	12 foot glass 1.8 mm I.D. 6mm O.D., 1% Dexil 300 on 80/100 mesh gas chrom Q.	same as for 1400
GC Injector Temperature (°C)	300	300
GC Detector Temperature (°C)	300	300
Typical Tempera- ture Program	150°C to 310°C at 6°C/ min	150°C to 320°C at 6°C/min
Carrier Gas	20 ml/min He	35 ml/min He
Fuel/Air	20 ml/min H <sub>2</sub> 200 ml/min	35 ml/min H <sub>2</sub> 350 ml/min air
Full scale Sensitivity	10 <sup>-11</sup> amps attenuation 16	10 <sup>-11</sup> amps attenuation 16
Sample Size	1-4 µl	1-4 µl
MS Separator Temperature (°C)	280	280
MS Ionization Energy (ev)	80	80
MS Resolution (10% Valley)	600	1000



collection, storage, and reduction were conducted with a Varian 620I computer, 12K core and 123K disk, two IBM compatible magnetic tape units, an ASR 33 teletype, and a Varian Statos 21 high speed plotter. Computer software permitted plotting of a "mass chromatogram" in Smythe, 1973 as well as selected single mass to charge ( $m/e$ ) ratio ion currents. The mass chromatogram (MC) permitted correlation of specific GC peaks with specific mass spectra and the single  $m/e$  plots permitted location of specific compound peaks in a maze of unresolved GC peaks.

Filter exhaust particulate samples were irradiated with UV light, using the same experimental setup used above to irradiate lead halide aerosols. Circles of Reeve Angel 934 AH glass fiber filter 9 cm in diameter, with either leaded or unleaded particulates collected, were irradiated for 10 hr at 32°C with 100 ml/min of dry CO<sub>2</sub> free air being swept through the irradiation chamber. The sweep gas was passed through a dry ice-acetone trap to collect any volatile condensible products. After irradiation, the filters were soxhlet extracted with freshly distilled diethyl ether and the extract concentrated for GCMS analysis as described above.

### C. Results and Discussion

a. Physical Characteristics - The results of all automobile exhaust particulate collection tests conducted after engine "breakin" are summarized in Table 21. Several observations can be made about these data:

(1) For collections made under similar conditions, the mass emission rates vary a great deal more from one run to the next for cyclone particulates than for filter particulates. The reasons for this are discussed below.

(2) With the exception of an initial breakin period for the monolith converter, the mass emission rate of particulates collected on the filter (30 MPH, non-leaded fuel) with a catalytic converter installed, while the mass emission rate of cyclone particulates is about the same for tests conducted at about the same mileage. Thus, the catalytic converters are effective in reducing total particulate emissions.

(3) The ether extractable material for filter particulates with a catalytic converter installed is about one-fourth to one-fifth of that with no converter installed. Thus, the catalytic converters are even more effective in reducing the ether ex-

Table 21

## Comparative Particulate Emission Tests (c)(d)

	mg/mi Collected			Ether Extractable from Filter		
	Filter No.	Filter	Cyclone	Mg/mi	%	Miles on Engine at End of Run
1. Monolith Converter (non-leaded indolene)	9	5.42	(a)	4.56	84.1	1180
	13	6.30	0.04	(b)	(b)	1370
	14	1.50	0.09	0.87	58.4	1535
	15	0.39	0.11	0.17	42.7	1640
	20	0.42	0.56	0.14	32.8	2185
	22	0.41	0.26	0.14	33.9	2450
2. Beads Converter (non-leaded indolene)	10	0.28	(a)	0.21	75.9	1270
	17	0.39	0.25	0.17	44.0	1870
	18	0.41	0.47	0.12	28.9	1975
	23	0.35	0.33	(b)	(b)	2560
	25	0.45	0.37	0.16	35.3	2770
3. No Converter (non-leaded indolene)	11	1.20	0.08	1.15	95.2	1490
	16	1.19	0.11	0.92	76.9	1745
	19	1.06	0.23	0.83	77.6	2080
	24	0.63	0.34	(b)	(b)	2665
4. No Converter (2.5 gm/gal leaded indolene)	26	24.50	0.51	0.75	3.1	2865
	27	22.80	8.69	(b)	(b)	2910
	28	25.30	2.54	(b)	(b)	2965
	29(d)	146.00	286.70	(b)	(b)	3010
	30	24.30	0.85	0.53	2.2	3070
	32	26.00	4.65	0.61	2.3	3130
	33(d)	182.40	1433.30	(b)	(b)	3175

(a) Not collected. (b) Not extracted. (c) All values for total exhaust.

(d) All values for steady 30 MPH, except filter samples 29 and 33, which were obtained at steady 60 MPH.

tractable organic content of filter particulates than in reducing total particulate emissions.

(4) The mass emission rate of filter particulates is about a factor of twenty higher when leaded gasoline is burned (30 MPH, no converter) than when non-leaded gasoline is burned under the same conditions, yet the ether extractable material is roughly the same. Thus, the mass of ether extractable organics associated with the filter particulates has little to do with whether the fuel is leaded or unleaded.

(5) Although the gasoline consumption rate per unit time almost exactly doubled for 60 miles per hour compared to 30 miles per hour with leaded fuel being burned, the corresponding filter particulate emission rate was about six times greater.

Figure 16 shows a cross-sectional view of a Reeve Angel 934AH glass fiber filter with leaded exhaust particulates collected on it. Although the average cross-sectional thickness of the filter is about 640  $\mu\text{m}$ , virtually all the particulates are trapped in the first 60  $\mu\text{m}$ . Thus, the first one-tenth of the filter thickness does essentially all the particulate filtering.

Figure 16

Cross Section of Filter with Collected Particulates and  
Clean Filter

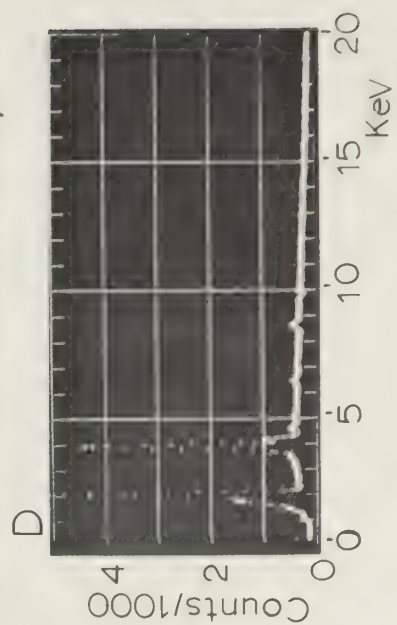
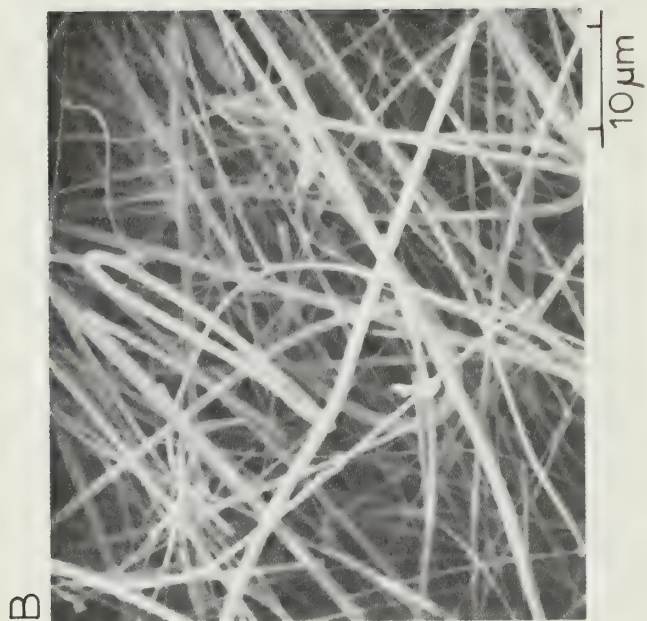
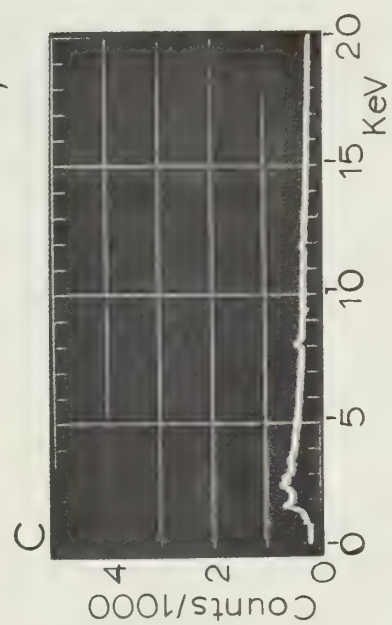
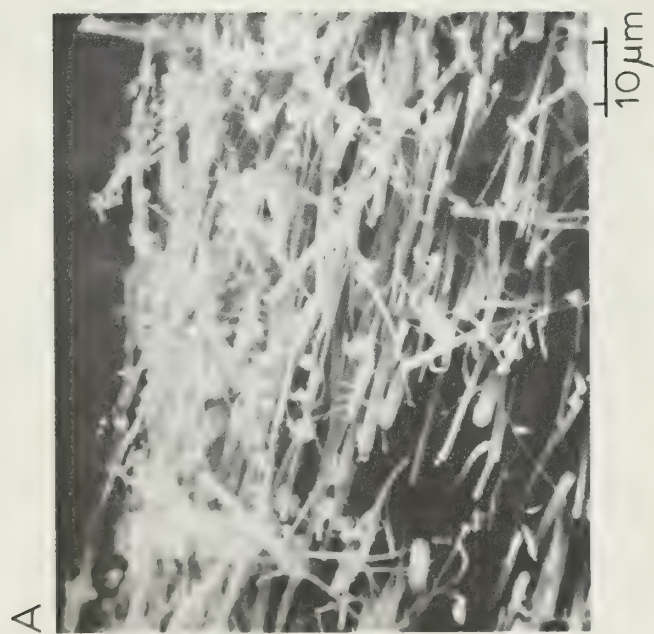
- (A) Cross Section of a Reeve Angel 934AH glass fiber filter with leaded exhaust particulates collected on it.
- (B) Clean Reeve Angel 934AH glass fiber filter.
- (C) X-Ray Spectrum of Scotch<sup>R</sup> double sided tape used to mount cyclone particulates for SEM Examination.

<u>Energy (KeV)</u>	<u>Element (line)</u>	<u>Comments</u>
1.7	Si(K <sub>α</sub> )	
2.6	Cl(K <sub>α</sub> )	
8.1	Cu(K <sub>α</sub> )	

- (D) Reeve Angel 934AM Glass Fiber Filter X-ray Spectrum

<u>Energy (KeV)</u>	<u>Element (X-ray line)</u>	<u>Comments</u>
1.5	Al(K <sub>α</sub> )	Background-specimen stub
1.7	Si(K <sub>α</sub> )	Major Component
3.7	Ca(K <sub>α</sub> )	Major Component
4.0	Ca(K <sub>α</sub> )	
4.5	Ti(K <sub>α</sub> )	Minor Component
6.4	Fe(K <sub>α</sub> )	Minor Component
8.6	Zn(K <sub>α</sub> )	Minor Component





The filter particulate loading was much higher for leaded runs than for non-leaded runs, as seen by SEM. Figures 17 and 18 show filter and cyclone particulates, respectively, with their corresponding energy dispersive x-ray spectra. These electron micrographs illustrate that the cyclone separator is very effective in separating particulates larger than a few micrometers, which would quickly fall out on the ground in the environment, from the 2  $\mu\text{m}$  or smaller particulates collected on the filter, which would stay air suspended or would be retained by the lungs when inhaled. Comparison of the x-ray spectra shows that the major components of the filter particulates are lead, bromine, and chlorine, the source of which would be the engine combustion process, while the major component in the cyclone particulates is iron, the most probable source of which would be rust in the exhaust system. By contrast, lead, bromine, and chlorine are very minor components in the cyclone particulates, while iron is a very minor component in the filter particulates. Thus, there is a fundamental difference in elemental composition between large and small particulates. It was noted above that there is a much greater variation in the emission rates for cyclone particulates than for filter particulates.

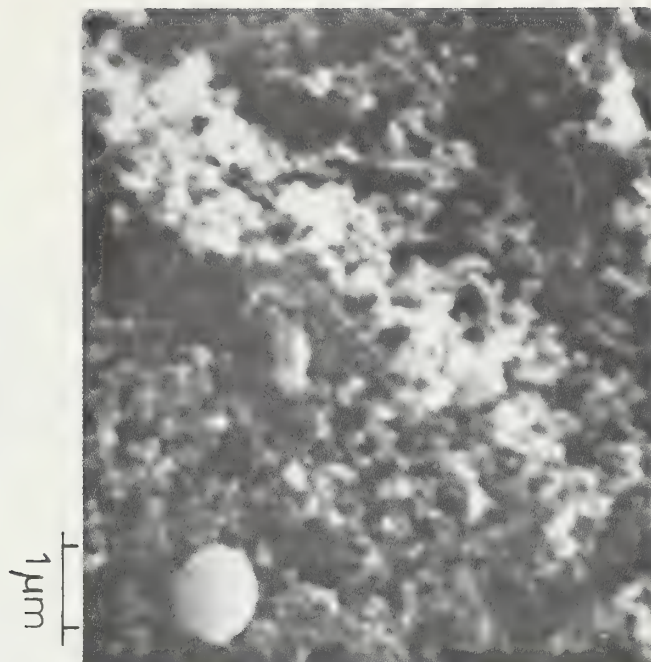
Figure 17

## Filter Particulates (Leaded Fuel, No Converter)

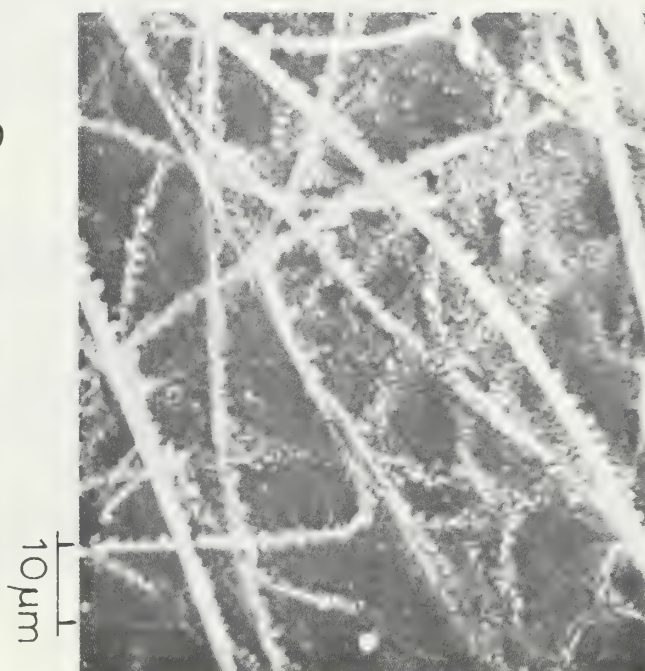
- (A) Filter Particulates. High magnification. One-hour collection at 30 MPH, leaded fuel.
- (B) Filter Particulates. Low magnification. Particulate loading on filter  $392 \mu\text{g}/\text{cm}^2$ . Same filter as (A).
- (C) X-ray Spectrum for (A) and (B)

<u>Energy</u>	<u>Element and Line</u>	<u>Comments</u>
1.5	Al( $K_\alpha$ ), Br( $L_\alpha$ )	
1.7	Si( $K_\alpha$ )	Background-filter
2.4	Pb( $M_\alpha$ )	
2.6	Pb( $M_\beta$ ), Cl( $K_\alpha$ )	Major Components
3.7	Ca( $K_\alpha$ )	Background-filter
4.0	Ca( $K_\beta$ )	Background-filter
6.4	Fe( $K_\alpha$ )	Minor Component
8.0	Cu( $K_\alpha$ )	Minor Component
10.5	Pb( $L_\alpha$ )	Major Component
11.9	Br( $K_\alpha$ )	Major Component
12.6	Pb( $L_\beta$ )	
13.3	Br( $K_\beta$ )	
14.7	Pb( $L_\gamma$ )	

A



B



C

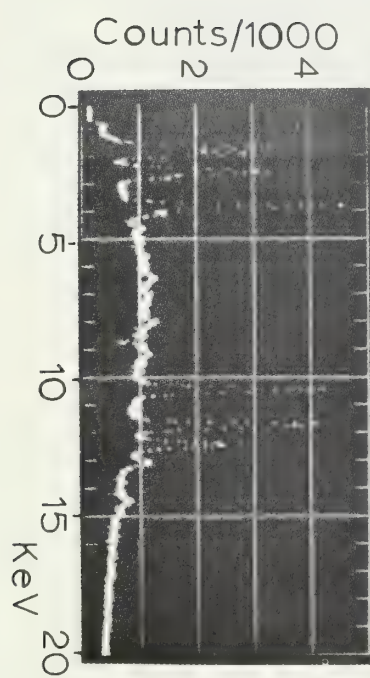




Figure 18

Cyclone Particulates (Leaded Fuel, No Converter)

(A) Cyclone particulates

(B) X-ray spectrum for (A)

<u>Energy (KeV)</u>	<u>Element and Line</u>	<u>Comments</u>
1.5	Al( $K_{\alpha}$ )	Minor component
2.3	S( $K_{\alpha}$ ), Pb( $M_{\alpha}$ )	
2.6	Cl( $K_{\alpha}$ )	
5.4	Cr( $K_{\alpha}$ )	Minor component
6.4	Fe( $K_{\alpha}$ )	Major Component
7.1	Fe( $K_{\beta}$ )	
10.5	Pb( $L_{\alpha}$ )	Minor Component
11.9	Br( $K_{\alpha}$ )	Minor Component
12.6	Pb( $L_{\beta}$ )	

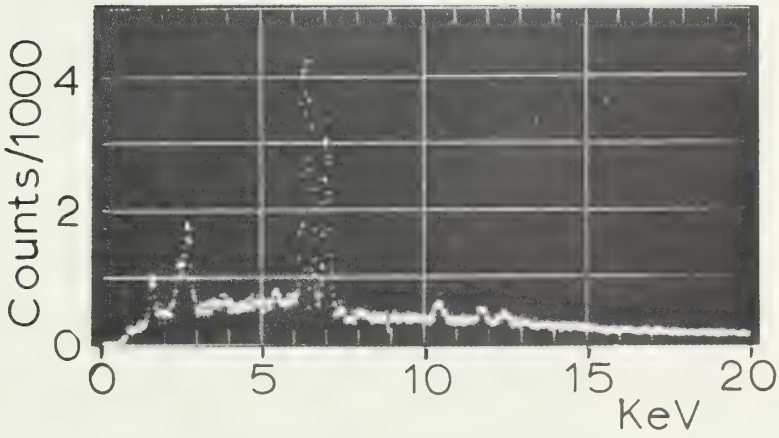


A



50 μm

B



These two observations suggest that formation of the sub-micrometer particulates depends more on non-variable factors, such as the running condition of the engine from one run to the next, while origination of the cyclone particulates depends more upon variable factors, such as the condition of the exhaust system from one run to the next, e.g., the extent of rust formation in the exhaust system.

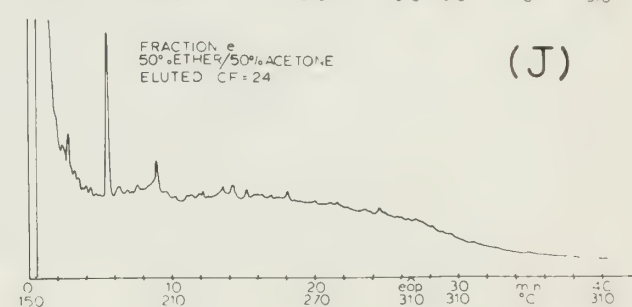
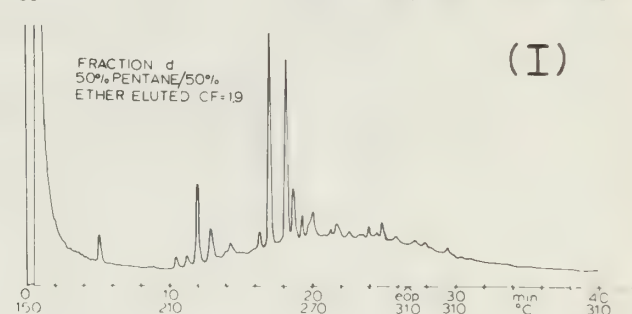
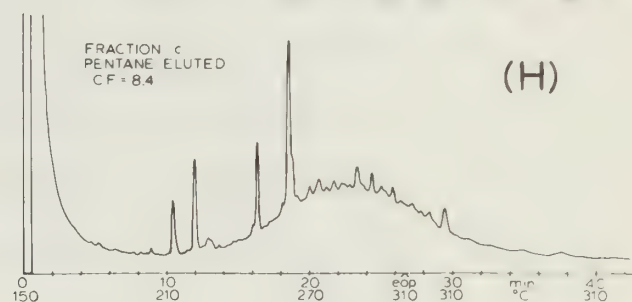
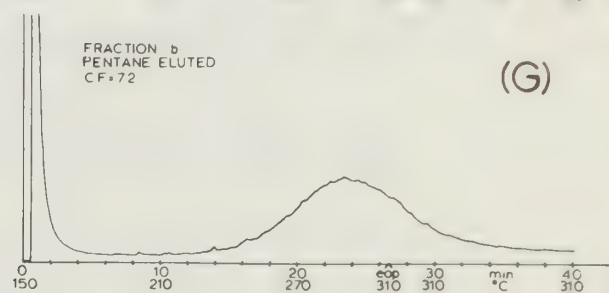
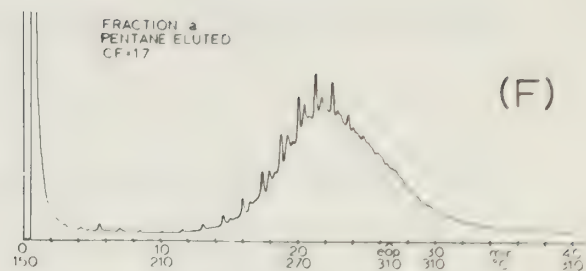
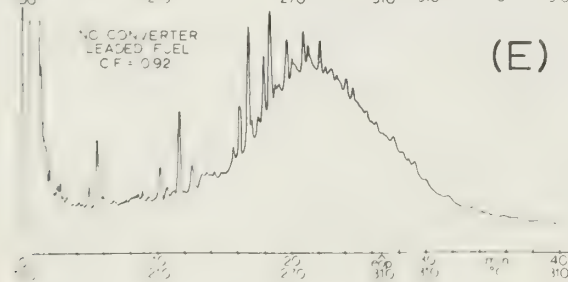
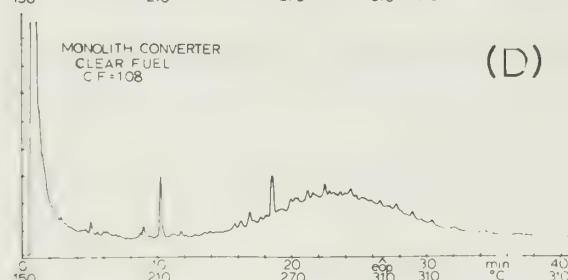
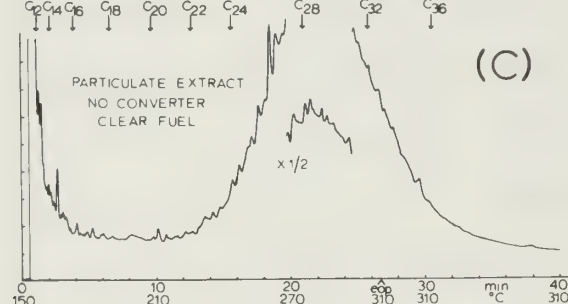
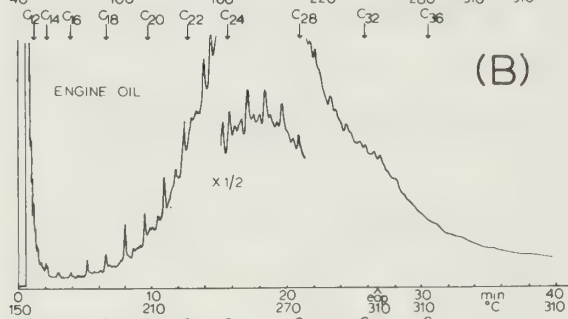
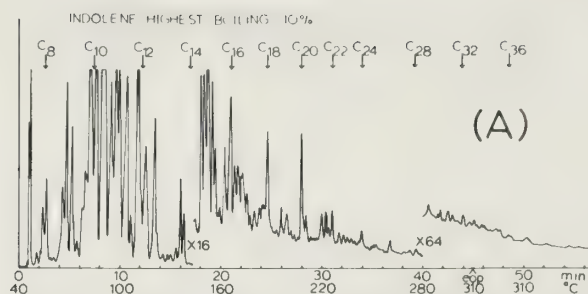
Comparison of the  $\text{BrK}_\alpha$  to  $\text{PbL}_\alpha$  intensity ratio in Figure 17 ( $\text{BrK}_\alpha/\text{PbL}_\alpha = 1.03$ ) to that obtained for  $\text{PbBr}_2$  ( $\text{BrK}_\alpha/\text{PbL}_\alpha = 1.52$ ) and for pure  $\text{PbBrCl}$  ( $\text{BrK}_\alpha/\text{PbL}_\alpha = 0.74$ ) shows that the filter fraction of the leaded exhaust particulates are definitely bromine rich compared to stoichiometric  $\text{PbBrCl}$ . This confirms previously reported findings in Moran et al., 1971 and 1972 of bromide rich exhaust particulates. The x-ray spectrum in Figure 3 was taken many hours after particulate collection and no large bromine loss has occurred as reported by previous studies in Ter Haar and Bayard, 1971; Robbins and Snitz, 1972.

b. GC Analysis of Fuel, Engine Oil, and Particulate Extracts - As shown by Figure 19, the GC's for the oil and the particulate extracts include a "hump" of literally hundreds of unresolved peaks for compounds in the molecular

Figure 19

GC's of Test Fuel, Engine Oil, Raw Particulate Extracts  
and LC Fractions

- (A) Indolene highest boiling 10%
- (B) 5% engine oil (Shell Super X) in n-pentane
- (C) Raw particulate extract, no converter, clear fuel.  
C.F. = 1.01
- (D) Raw particulate extract, monolith converter, clear  
fuel. C.F. = 1.08
- (E) Raw particulate extract, no converter, leaded fuel.  
C.F. = 0.92
- (F) through (J) LC Fractions of (E)
- (F) LC Fraction a, pentane eluted. C.F. = 1.7
- (G) LC Fraction b, pentane eluted. C.F. = 7.2
- (H) LC Fraction c, pentane eluted. C.F. = 8.4
- (I) LC Fraction d, 50% pentane/50% ether eluted.  
C.F. = 1.9
- (J) LC Fraction e, 50% pentane/50% acetone eluted.  
C.F. = 2.4



weight range of 300 to 500. The bulk of the components in the particulate extract "hump" have a GC retention time greater than that of straight chain aliphatic C-22 and a median retention time equivalent to that of straight chain aliphatic C-29. By comparison, less than 0.1% of the Indolene test fuel has a GC retention time greater than C-22, while the median retention time of the engine oil hump is shifted about three carbon numbers lower to C-26. This does not imply that unburned fuel or engine oil do not contribute to exhaust particulates, but it does show that if unburned fuel and engine oil are significant contributors, then the lower molecular weight compounds are burned in preference to those of higher molecular weight.

The concentration factor (C.F.) given for each particulate extract GC is a normalization parameter to allow quantitative comparison of GC peak areas. The C.F. includes correction for sample collection time, % of the filter extracted, sample solution volume, GC sample volume, and GC detector response. The GC area from time 4 minutes to time 40 minutes gives a ratio of 3.5 for ether-extractable organics for the no converter-clear fuel to monolith converter-clear fuel system. This



confirms the conclusion from the data in Table 22, that the catalytic converters are effective in significantly reducing ether extractable organics in the exhaust particulate matter.

The corresponding GC area ratio for no converter-clear fuel to no converter-leaded fuel ether extract is 1.2, implying that the presence of lead may reduce the amount of ether extractable organics. Using the Pregl method of combustion with a Sargent Micro Combustion Apparatus, quantitative analysis for carbon remaining on the filter after extraction gave a ratio of 1.25 for unleaded sample to leaded sample non-extractable carbon. Thus, the ratio of ether extractable carbon to non-extractable carbon is about the same, even though the available particulate surfaces are much larger in the case of the leaded particulates. This rules out adsorption of organics from the gaseous phase by the particulate surfaces as a significant contribution to the total organic matter extracted, and suggests that the ether extractable organics are to be regarded as products of incomplete carbonization.

c. GC and UV-Visible Analysis of LC Fractions -  
Fractionation of the raw particulate extracts on activated

Table 22

UV-Visible Wavelength Maxima in Liquid Column Chromatographic c Fractions (Spectra in Figure 25)

Sample:	Wavelength (1)	Maxima (nm) (2)	(3)	Possible Source (a) and Comments	( $\lambda_{\text{max}}$ )
	231	231	230	Solvent cutoff	
			257		
	263	260	264	(b) Chrysene	(267)
			270		
	281		288	(b) Benzo(a) anthracene Fluoranthene	(288)
	293	293			(299)
	301	302	301	(b) Benzo(b)fluoranthene	(302)
	305	306			
	315				
	327				
	335	336		(b) Benzo(e)pyrene	(332)
	341			Pyrene	(336)
	365			Benzo(ghi)perylene	(362)
	381			Benzo(c)acridine	(384)
	386			(b) Benzo(a)pyrene	(384)
	406				
		415	413		
				Anthanthrene	(430)
	433	432	433	Perylene	(434)

- 
- (a) Reference: Union Carbide PSM-1016, 1972  
 (b) Known carcinogen (Hoffmann and Wynder, 1968)

silica gel columns resulted in the UV-visible spectra shown in Figure 20 for the first four fractions of each of the extracts discussed above, and in the GC's shown in Figure 10F through J for the leaded fuel-no converter particulate extract. The UV-visible spectra of each LC fraction do not by themselves provide much information about the composition of the fraction, because the GC's show that the LC fractions, like the raw extracts, are still very complex mixtures. As mass spectral data will later show, LC fraction c contains polynuclear aromatic hydrocarbons (PNA's). Table 22 lists the UV-visible absorption maxima of some PNA's, several of which coincide with maxima seen in the LC fraction c spectra. The presence of some of these PNA's is later confirmed by mass spectral data.

A sample handling recovery and background contamination study, which included every step in the experimental procedure from collection to GCMS analysis, was run on the standard mixture of straight chain aliphatic hydrocarbons and polynuclear aromatic hydrocarbons. The average recovery was 59% for aliphatics and 50% for PNA's. Contaminants picked up during a two-hour blank collection of filtered background air included trace levels of diethyl phthalate, di-iso-butyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, and one unidentified

Figure 20

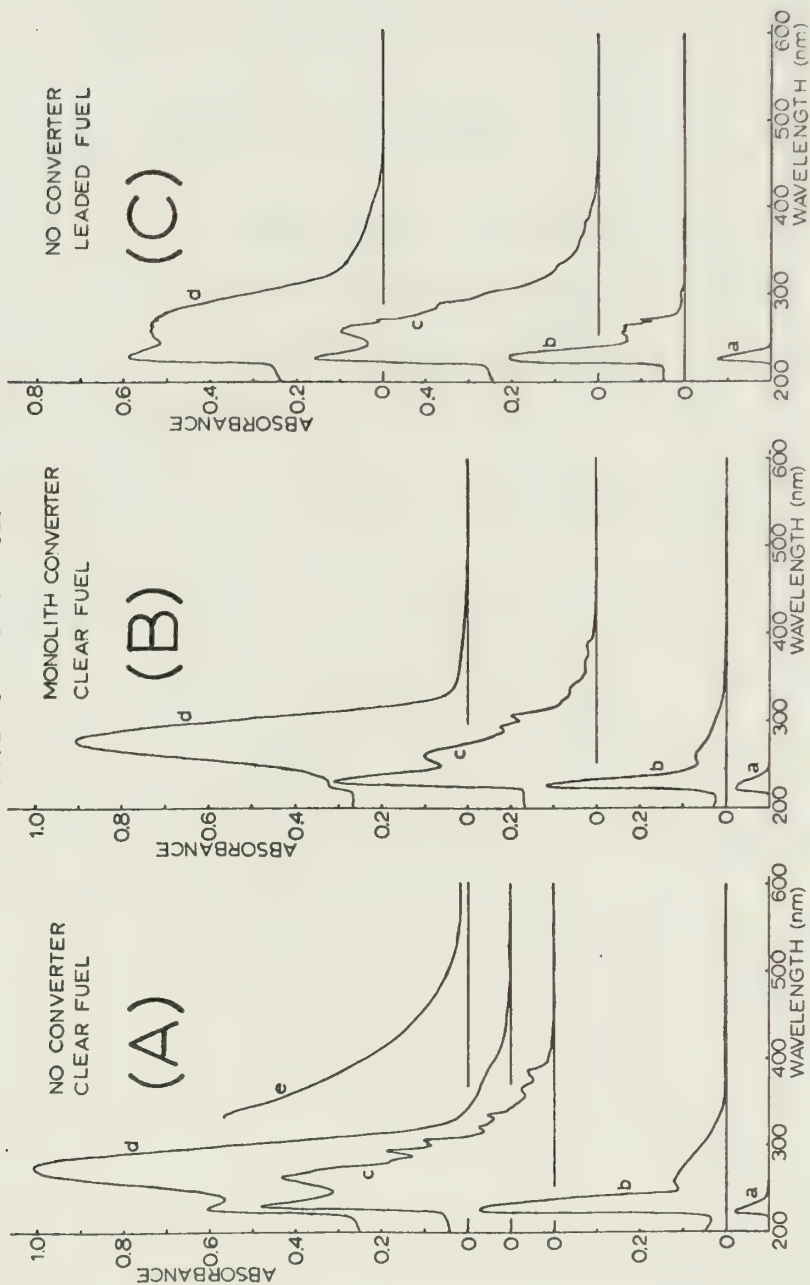
UV-Visible Absorption Spectra of Liquid Column Chroma-  
tographic Fractions

Particulate Extract Source

- (A) No Converter, Clear Fuel
- (B) Monolith Converter, Clear Fuel
- (C) No Converter, Leaded Fuel

FRACTION	ELUTED BY	*DILUTION FACTOR		
		A	B	C
a	PENTANE	1.2	0.9	2.5
b	PENTANE	6.0	1.0	2.6
c	PENTANE	5.6	3.0	20.0
d	50% PENTANE/ 50% ETHER	200	16.0	17.0
e	50% ETHER/50% ACETONE	400	-	-

\*RELATIVE TO FRACTION VOLUME = 5 ml.





compound. No detectable contaminants were introduced during LC fractionation.

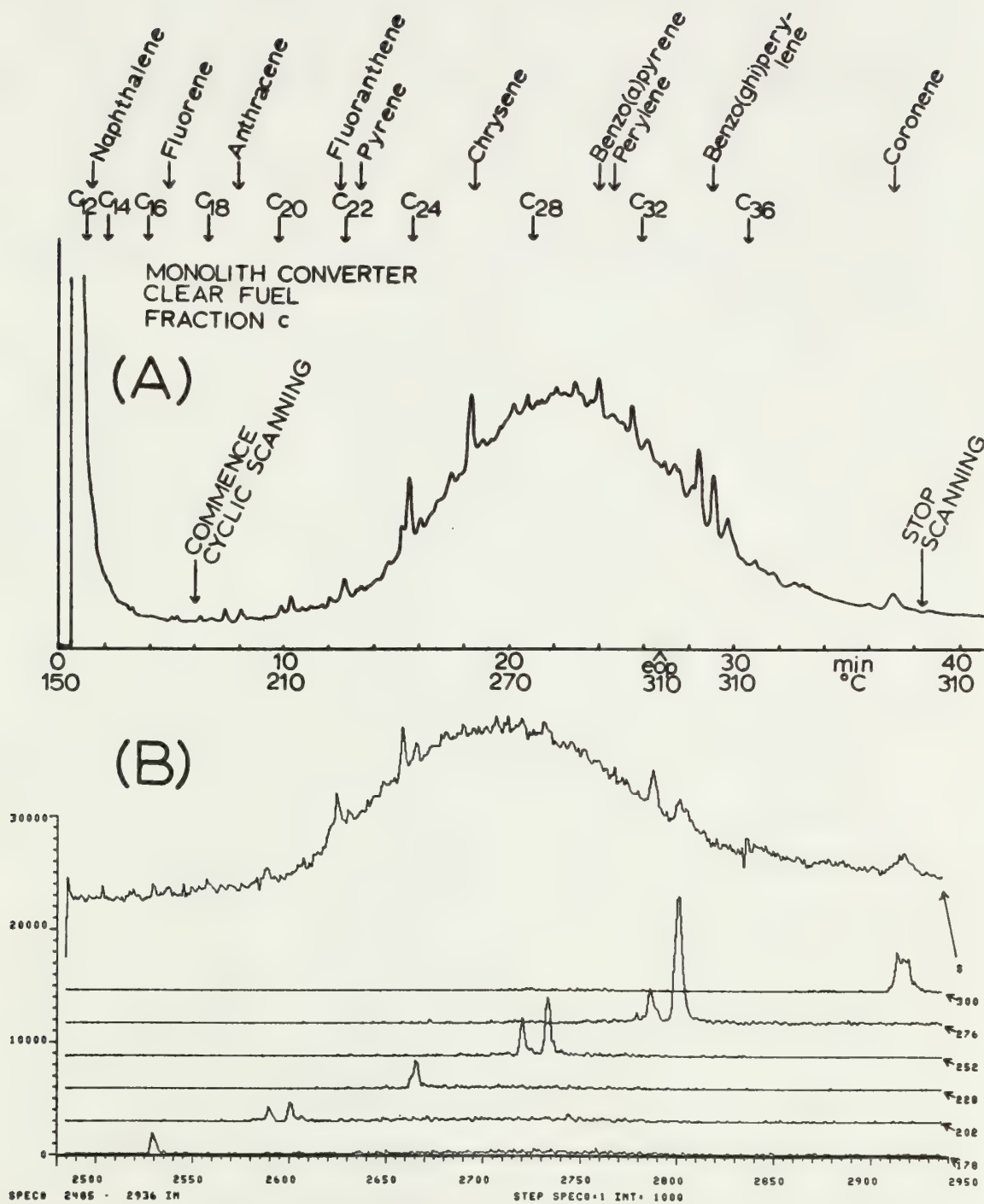
d. GCMS Analysis of Representative Samples - In a manner similar to that previously described in Karasek, 1973, representative mass spectral data are presented as cyclic scanning mass chromatograms, including a total ion current plot and specific  $m/e$  ion current plots versus spectrum number. Space limitations preclude presentation of individual mass spectra. Identifications of unknowns are based on comparison with mass spectra obtained with the same instrument from known compounds, comparison of the eight most intense peaks with a reference tabulation from the Eight Peak Index, 1970, data system search of the Aldermaston mass spectral library, and comparison of the GC retention indices in Harris and Habgood, 1966, p. 155.

The usefulness of cyclic scanning mass spectroscopy in locating specific components "hidden" in a myriad of unresolved GC peaks is illustrated by Figure 21, in which the single  $m/e$  ion plots correspond to the molecular weights of polynuclear aromatics used in the standard test mixture for daily check of the GC response. These included a hracene (MW = 178), fluoranthene and pyrene

## Figure 21

GC and MC Showing Location of Polynuclear Aromatics "Hidden"  
in GC Envelope

- (A) GC of LC fraction c (monolith converter, clear fuel). Varian 1400 GC
- (B) MC of (1). Varian MAT-111 GCMS System



(MW = 202), chrysene (MW = 228), benzo(a)pyrene and perylene (MW = 252), benzo(ghi)perylene (MW = 276), and coronene (MW = 300). Moreover, except for perylene and one of the m/e 276 peaks, the GC retention indices of the single ion peaks coincide with the GC retention indices of the above compounds having the corresponding molecular weight.

An MC of typical LC fraction a is shown in Figure 22. Fragment ions with m/e 57, 85, and 113 are characteristic of saturated aliphatic hydrocarbons. As the GC and single ion plots show, the LC fraction a is an extremely complex mixture with the GC retention times and mass spectra of the most distinct peaks in the GC corresponding to the indicated straight chain aliphatic hydrocarbons.

Typically, LC fraction b was not very well defined, but probably consisted of branched chain aliphatics, unsaturated aliphatics and small ring aromatics substituted with aliphatic side chains.

The GC and MC of a typical LC fraction c, derived from particulates with no converter installed and unleaded fuel being burned, are shown in Figure 23. Single m/e ion plots corresponding to the molecular weights of known PNA's are included in Figure 23.

Figure 22

GC and MC of Typical LC Fraction a

- (A) GC of LC Fraction a, beads converter, clear fuel  
Varian 1400 GC
- (B) Mass Chromatogram of (A) Varian MAT-111 GCMS System

<u>Peak Number</u>	<u>Identification or Comments</u>
a	n-Hexadecane
b	n-Heptadecane
c	n-Octadecane
d	n-Nonadecane
e	n-Eicosane
f	n-Heneicosane
g	n-Docosane
h	n-Tricosane
i	n-Tetracosane
j	n-Pentacosane
k	n-Hexacosane
l	n-Heptacosane
m	n-Octacosane
n	n-Nonacosane
o	n-Tricontane
p	n-Hentricontane
q	n-Dotriacontane
r	n-Tritriacontane



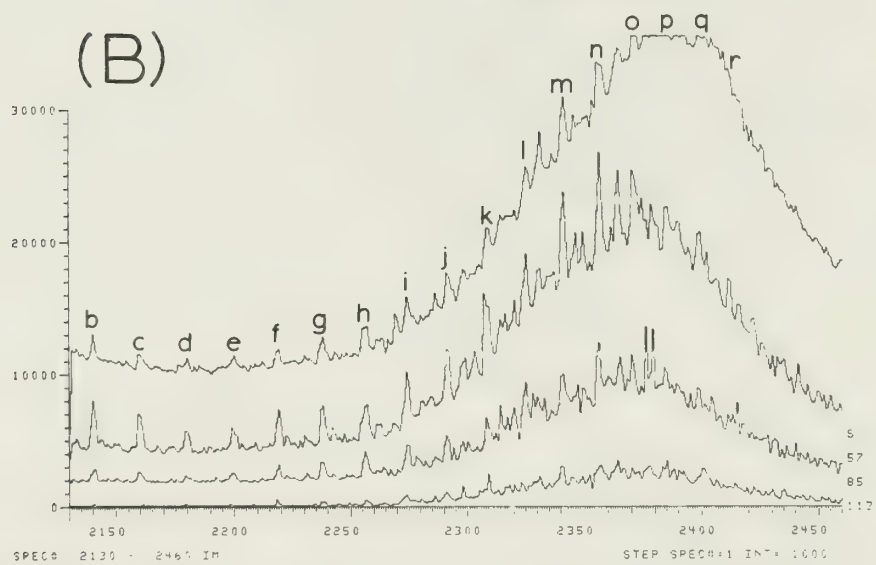
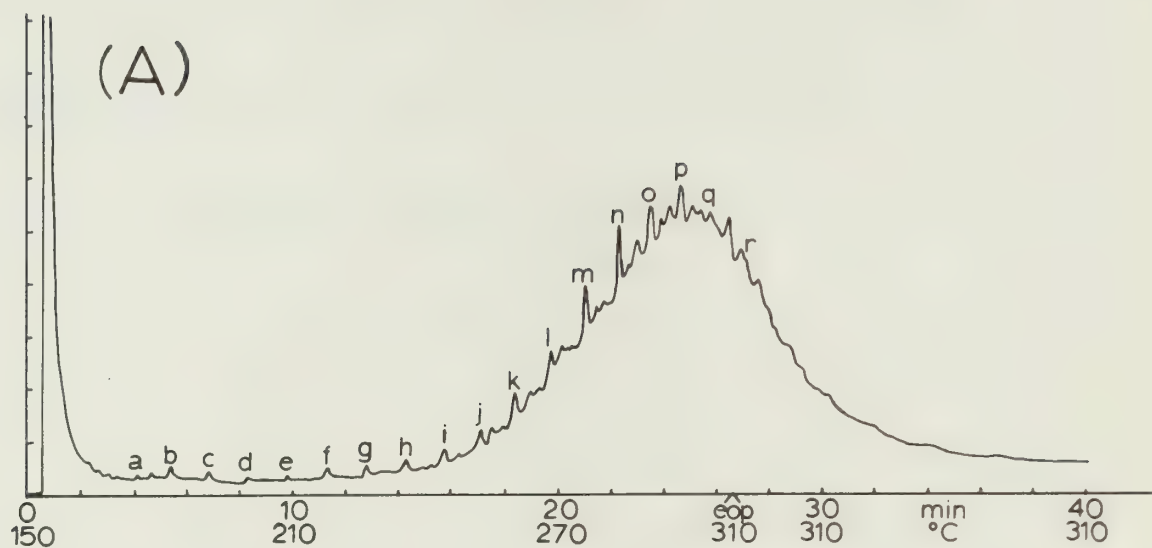


Figure 23

GC and MC of Typical LC Fraction c

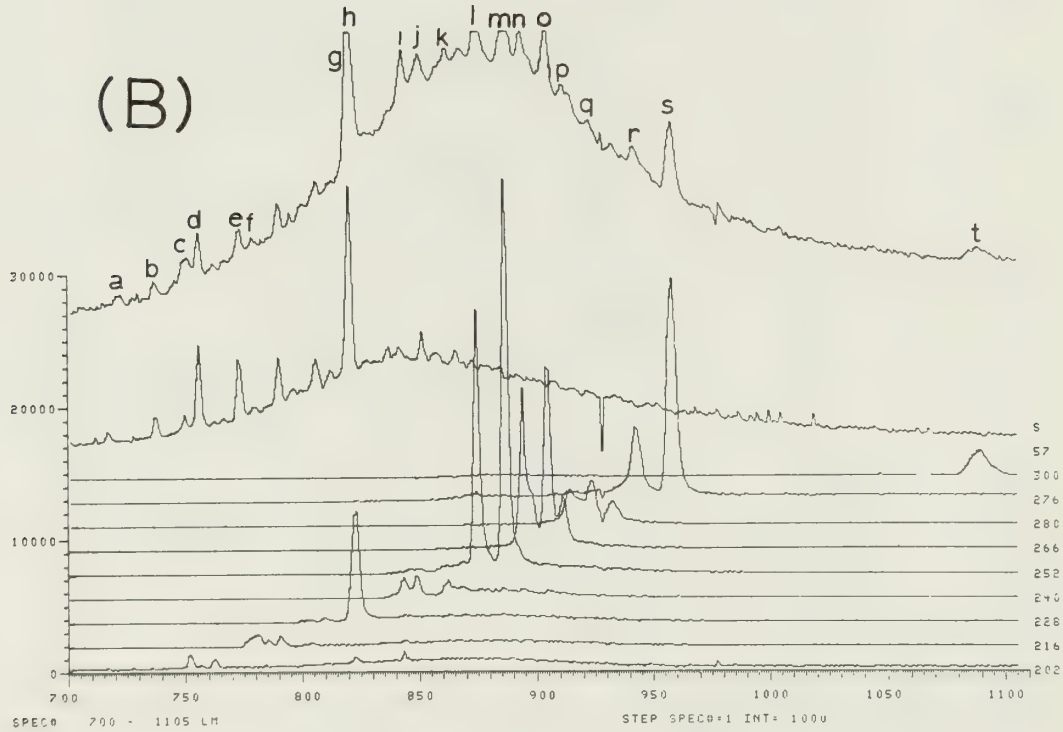
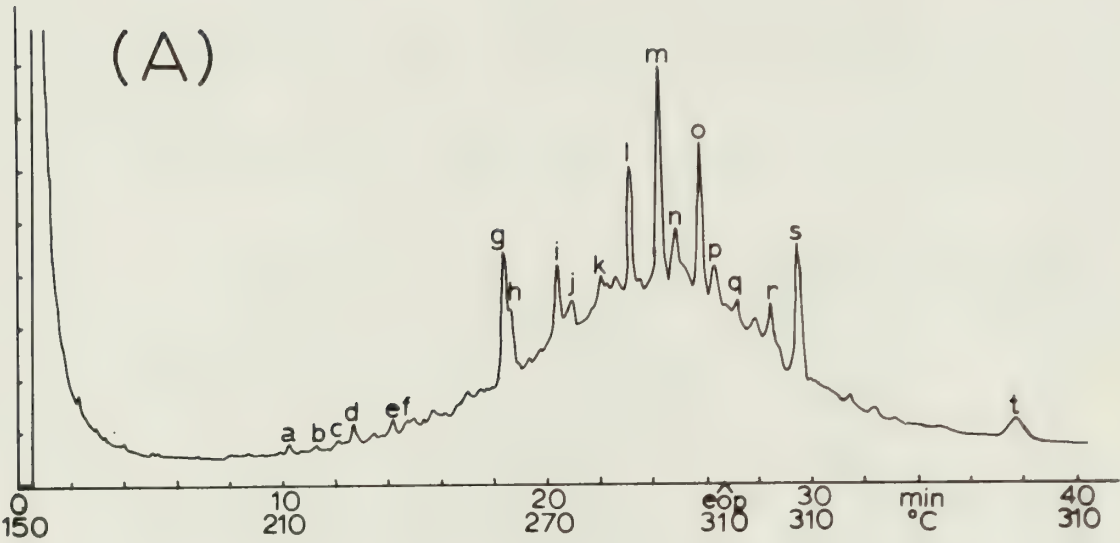
(A) GC of LC fraction c, no converter, leaded fuel.  
Varian 1400 GC

(B) MC for (A). Varian CH-7 Mass Spectrometry

Peak Number	Retention Index	Identification or Comments
a	2034	Di-n-butyl phthalate
b	2102	Branched chain saturated hydrocarbon
c	2166	Fluoranthene
d	2196	Branched chain hydrocarbon
(a)e	2300	Oxygenated. F.P. similar to 1,1-dihexoxyethane
f	2333	Similar to methyl pyrene
g	2595	Di-n-octyl phthalate
(b)h	2632	Chrysene
i	2774	Monomethyl benzo(a)anthracene or monomethyl chrysene
j	2806	Unidentified PNA, $M^+$ mass 242
k	2903	F.P. similar to 9,10-dimethyl benzo(a)anthracene
l	3000	F.P. similar to benzo(a)pyrene. Retention index too low for benzo(e)-pyrene or perylene
(b)m	3086	Benzo(a)pyrene
n	3137	Monomethylbenzpyrene
o	3215	Monomethylbenzpyrene
p	3254	Monomethylbenzpyrene. GC retention index same as 10-methylbenzo(a)-pyrene
q	3317	Mixture of two PNA's
r	3415	F.P. similar to 1,12-benzoperylene
s	3488	Benzo(ghi)perylene
t	-	Coronene

(a) F.P. = Fragmentation pattern

(b) Known carcinogen, Hoffmann and Wynder, 1968.



The GC and MC of a typical LC fraction d are shown in Figure 24. Most of the compounds identified in this fraction are oxygenated. It is not known whether all the phthalates appearing in this fraction are due solely to background air contamination, or are partially contributed by engine combustion products. The source of triphenyl phosphate and several methyl substituted isomers is probably from antioxidants in the motor mix antiknock solution added to the indolene fuel. Common antioxidants in antiknock packages include tricresyl phosphate, cresyl diphenyl phosphate, and methyl diphenyl phosphate, Fritsch, 1972.

Like LC fraction b, the typical LC fraction e contained hundreds of components all in low concentrations, resulting in few identifiable peaks. As Figure 24(J) shows, fraction e appears to contain the bulk of the lower molecular weight components of the raw particulate extract. To be so strongly retained by the LC column, these components almost surely must be oxygenated.

Typically LC fraction f did not give much of a GC response, even though there was definitely organic material present. Either the compounds present were so highly oxygenated that they gave a very low F.I.D. response, or were retained by the GC column.

Figure 24

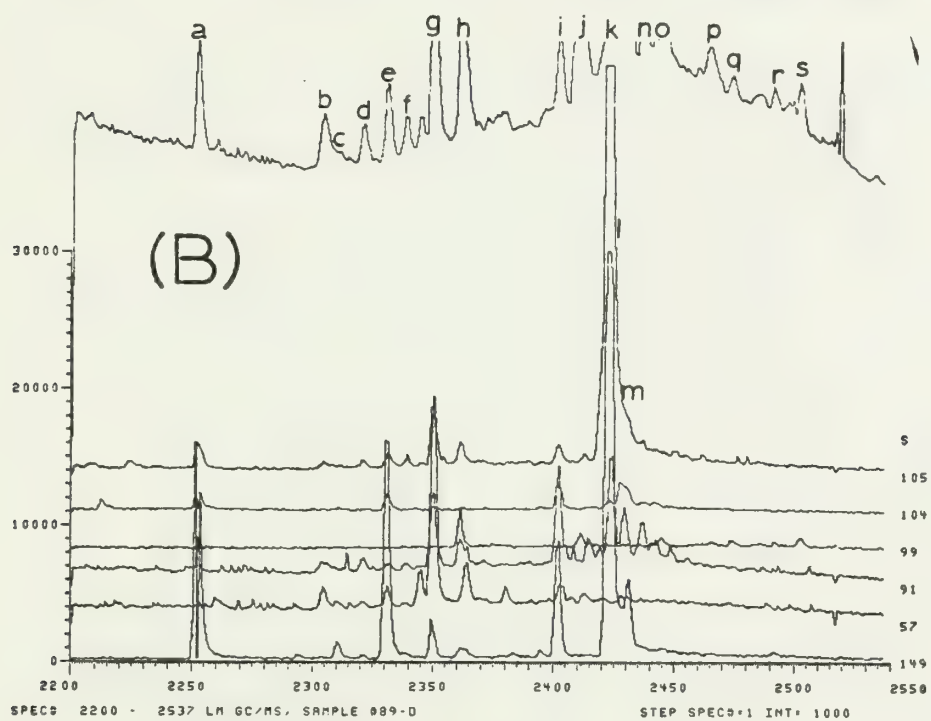
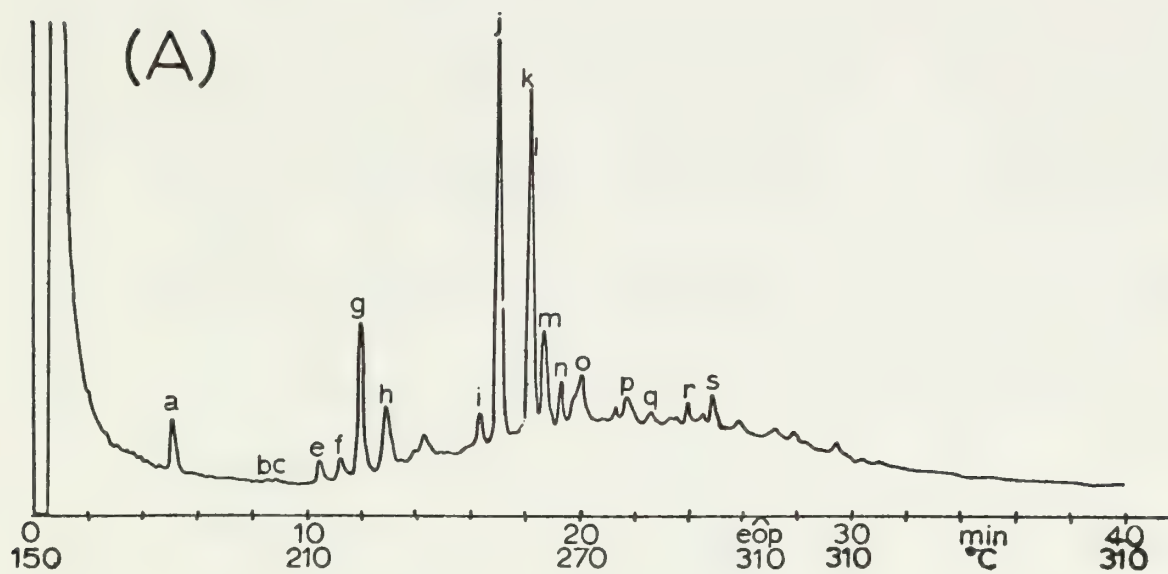
GC and MC of Typical LC Fraction d

(A) GC of LC fraction d, no converter, leaded fuel.  
Varian 1400 GC

(B) MC for (A). Varian CH-7 Mass Spectrometer

Peak Number	Retention Index	Indentification or Comments
a	1676	Diethyl phthalate
b	1898	F.P. similar to beta-capryophyllene
c	1919	Di-iso-butyl phthalate
d	1970	F.P. similar to Benzo(c)cinnoline
e	2022	Di-n-butyl phthalate
f	2070	F.P. similar to substituted benzoic acid
g	2122	Unidentified, m/e (% base): 134(100), 57(43), 107(38), 79(34), 41(33), 85(21)
h	2178	Unidentified, m/e (% base): 82.5(100), 55(32), 134(29), 79(19), 98(18), 107 (14), 166(14), Oxygenated
i	2415	Oxygenated. F.P. similar to 2,6-di- tert-butyl hydroquinone, or nonylphenol
j	2462	Triphenyl phosphate
k	2554	Di-n-octyl phthalate
l	2559	Monomethylsubstituted triphenyl phosphate
m	2595	Trimethylsubstituted triphenyl phosphate
n	2641	Dimethylsubstituted triphenyl phosphate
o	2697	Benzanthrone
p	2829	Unidentified, m/e (% base): 244(100), 215(43), 202(33), 258(27), 230(22). Appears to be mixture of several isomers.
q	2906	Unidentified, m/e (% base): 256(100), 200(45), 55(36), 99.5(34), 257(23)
r	3029	Unidentified, m/e (% base): 176(100), 204(95), 248(70), 87.5(66), 75(31), 150(28)
s	3106	Unidentified, m/e (% base): 254(100), 112.5(49), 226(43). Appears to be oxygenated PNA





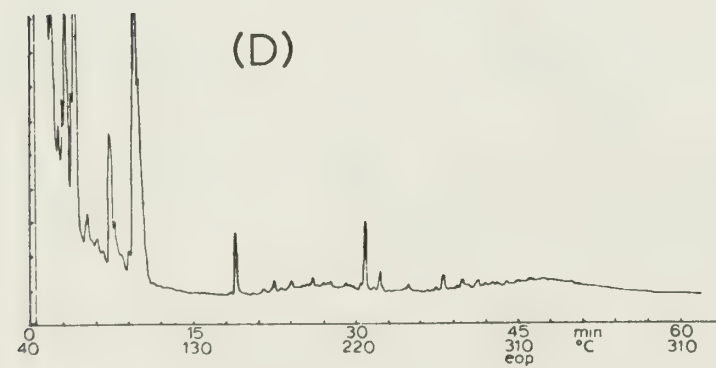
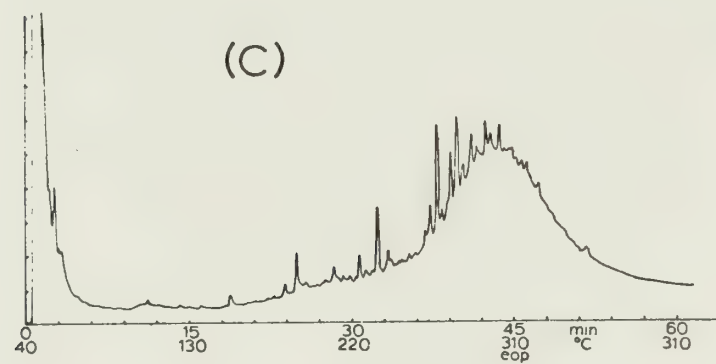
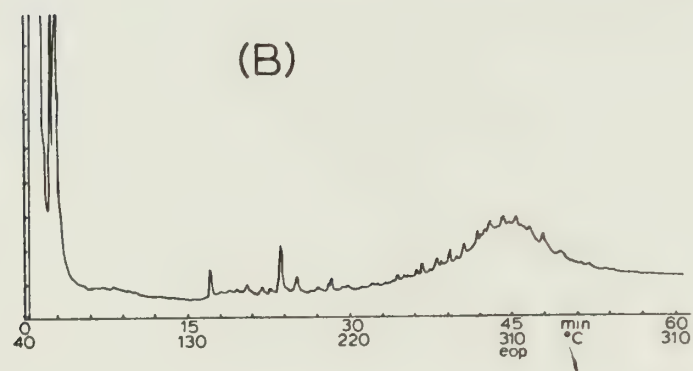
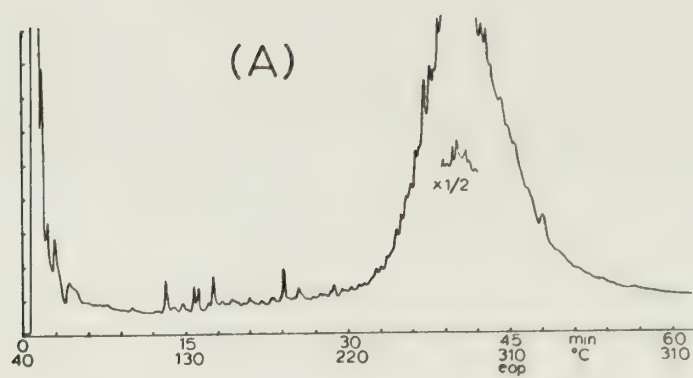
There is no doubt about the environmental significance of the PNA fraction, because of the presence of known or potentially carcinogenic compounds. What is not known, however, is the environmental significance of the oxygenated LC fractions d, e, and f, which constitute not only a larger portion of the particulate extract than the PNA's, but also contain hundreds of unidentified compounds of questionable health hazard effects. The composition of the more polar oxygenated compounds associated with automobile exhaust particulates should be investigated further.

e. UV Irradiation of Exhaust Particulates - As shown in Figure 25, irradiation of the filter exhaust particulates with ultraviolet light causes a dramatic reduction of the high molecular weight "hump" in the GC of the unfractionated particulate ether extract. There appear to be significant differences between irradiating non-leaded and leaded particulates. The high molecular weight "hump" is less completely degraded in the non-leaded case than in the leaded case. Irradiation of leaded particulates results in a larger number of GC peaks in the intermediate molecular weight region, indicating that there may be a fundamental difference in both the rate of degradation and in the degradation products.

## Figure 25

Effect of UV-Irradiation on Organics Associated with Exhaust  
Particulates

- (A) Unfractionated particulate extract, non-leaded gasoline, no converter. Varian 1800 GC
- (B) Particulate extract after filter irradiated 10 hours with UV light at  $6.3 \text{ mWatt/cm}^2$  (3000-4000 Å). Varian 1800 GC
- (C) Same as (A), except leaded gasoline burned
- (D) Same as (B)



Surprisingly, GCMS analysis of the ether extract of leaded particulates after irradiation with UV light did not reveal the presence of any halogenated hydrocarbons. Energy dispersive x-ray analysis of the particulates before irradiation indicated a bromine to lead ratio of 1.39, with irradiation for 10 hours at 6.3 mwatts/cm<sup>2</sup> causing the ratio to be reduced to 1.35. Assuming  $\text{PbBr}_{1.39}\text{Cl}_{0.61}$  as the principal compound being decomposed and assuming that bromine accounts for most of the halogen lost, this represents about a 2.0% loss of total halogen, compared to 1.4% predicted (PR3, Figure 18, page 56) for laboratory pure aerosols of the same composition. Assuming all of the non-ether extractable particulate matter irradiated (160.5 mg) was  $\text{PbBr}_{1.39}\text{Cl}_{0.61}$  indicates that 2.1 mg, or 13.1  $\mu\text{moles Br}_2$  were released. Assuming an average molecular weight of 400 for the ether extractable material present (5.2 mg) indicates that about 13  $\mu\text{moles}$  of organic matter was initially available for halogenation. Thus, for the total irradiation period, the mole ratio of available free halogen to organics to be halogenated was roughly one to one. The lack of halogenated organics being detected in the particulate extract, or recovered in the dry-ice acetone cold trap, indicates that either photodecomposition



of lead halides and subsequent halogenation of organics is much slower than photochemical decomposition of the organics, or that the halogenated products are themselves decomposed to very volatile products such as halomethanes. The photodecomposition of automobile exhaust particulates, both with leaded and unleaded gasoline being burned, should be investigated further.

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## B. Soil Deposition--Available Soil Lead

### 1. Capacity of Selected Illinois Soils to Remove Lead from Aqueous Solution

#### Background

Lead is being added to soil as lead halides, hydroxides, oxides, carbonates and sulfates when tetraethyl and tetramethyl lead is added to automotive fuels. Habibi, 1970; NAS, 1972; Ter Haar and Bayard, 1971; Zimdahl and Arvik, 1972. Lead may also be added to soils in lead arsenate insecticides and as an impurity in fertilizers. Schuck and Locke, 1970. Future additions of lead may result when effluents and sludges of municipal and industrial wastes are disposed of on land.

Broadbent and Ott, 1957 identifies soil pH, soil texture, percent organic matter, cation concentration and soil drainage as factors which determine the mobility of cations in soils. Zimdahl, Arvick and Skogerboe, 1973 found an increase in the soils ability to sorb lead with increasing C.E.C., pH and organic matter content.

This report presents data from a series of experiments designed to evaluate the effect of soil parameters on the capacity of soils to sorb Pb as  $\text{PbCl}_2$  from aqueous solutions. For these experiments Illinois soils (Table 23)

Table 23  
Properties of Selected Illinois Soils

	Cec	pH	P <sub>i</sub>	% O.M.	Pb Sorption Capacity, $\mu\text{g Pb/g}$
1. Bloomfield Loamy Sand	2.3	6.1	56	2.1	2,300
2. Cisne Silt Loam	6.8	5.23	63	2.1	2,894
3. Cisne Silt Loam	8.5	6.5	96	2.5	9,258
4. Cisne Silt Loam	7.9	6.3	63	2.3	6,115
5. Flanagan Silt Loam	21.5	6.4	13.4	6.1	19,900
6. Sidell Silt Loam	15.9	6.7	7.6	4.8	15,250
7. Drummer	30.3	6.5	39	6.7	24,350

were selected to provide a range in C.E.C., organic matter content, pH and soluble P (Bray P<sub>1</sub>). The sorption capacity of the soils for Pb was measured via absorption isotherms and in column leaching experiments.

## 2. Experimental Procedures

One gram of soil was shaken at constant temperature (25°) with 50 ml of PbCl<sub>2</sub> solution. Initial Pb concentrations ranged from 125 ppm Pb<sup>+2</sup> to 500 ppm Pb<sup>+2</sup> as PbCl<sub>2</sub> in 1 mM CaCl<sub>2</sub>. The amount of Pb removed from solution (x) was calculated as the difference between initial and equilibrium concentration after 24 hours of shaking. A plot of the amount of Pb removed per gram of soil (x) vs. equilibrium concentration (C<sub>eq</sub>) produced Langmuir type isotherms (Figures 26 and 27).

A linear plot of the Langmuir isotherm, Kuo and Lotse, 1972, where C<sub>eq</sub>/x is plotted against C<sub>eq</sub> was used to calculate an adsorption maximum. It was recognized that processes other than adsorption; i.e., precipitation and/or complexation, may also be involved in the sorption of Pb by soils. These additional processes should not prevent the use of a Langmuir plot.

Sorption capacities obtained from Langmuir plots were compared to the capacity of soils to remove lead from solution upon leaching with aqueous solutions of PbCl<sub>2</sub>.

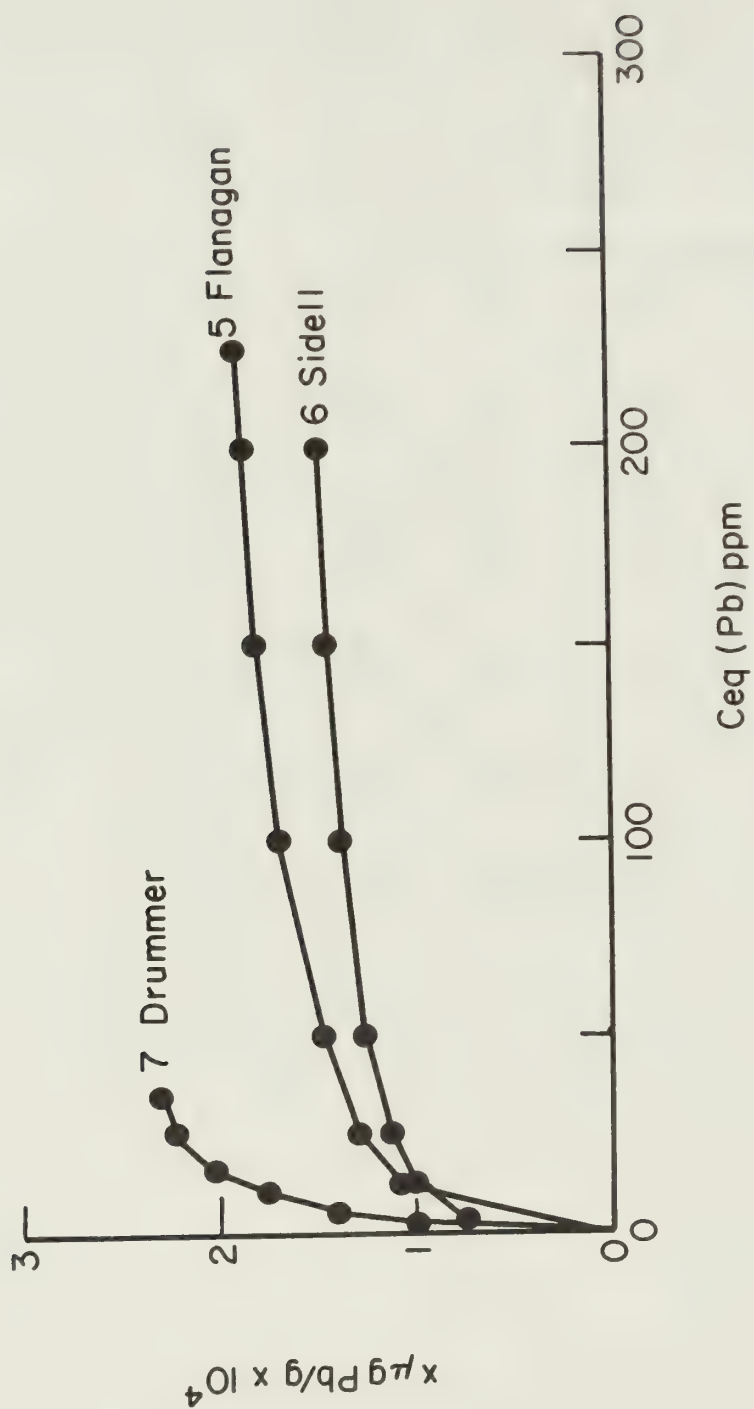


Figure 26

Sorption Isotherms of Selected Illinois Soils for Pb  
(Dark Prairie Soil - Mollisols)

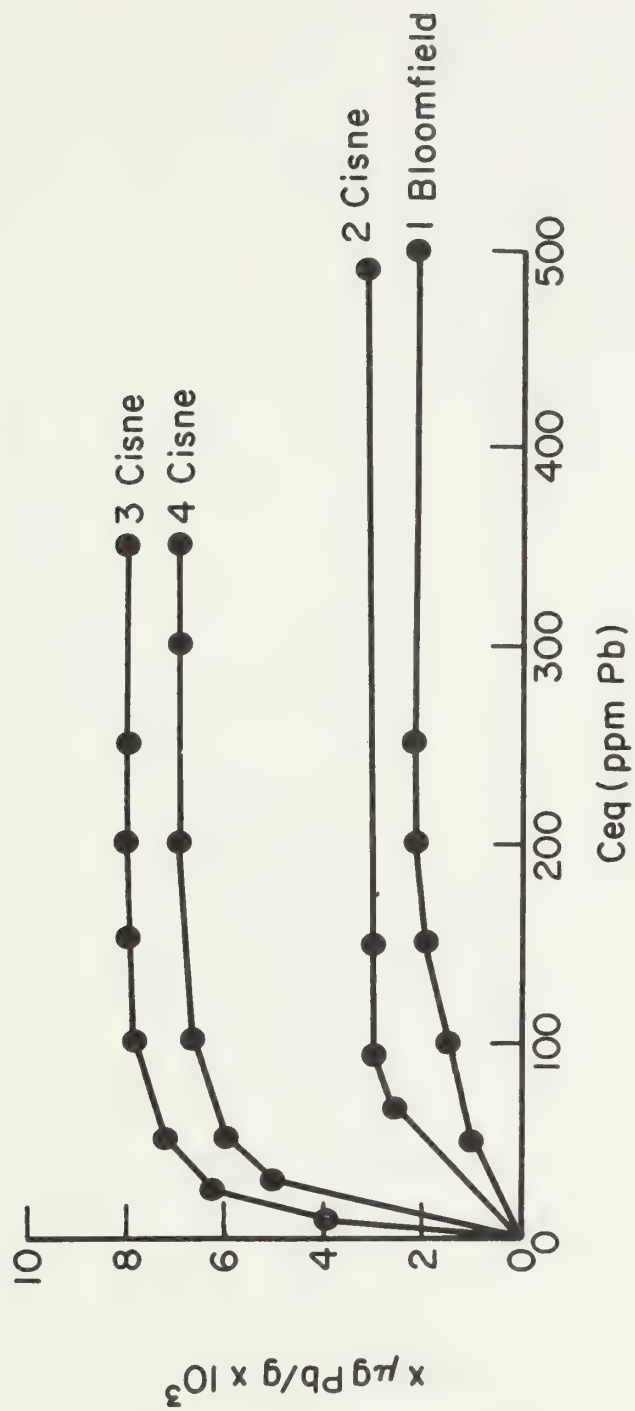


Figure 27  
Sorption Isotherms for Selected Illinois Soils for  
Pb (Light Colored Prairie Soils)



In the leaching experiments, 10 grams of soil was leached with 100 ppm  $\text{PbCl}_2$  in 1 mM  $\text{CaCl}_2$ . The effluent was collected and analyzed for Pb until its concentration in the effluent was equal to 100 ppm  $\text{Pb}^{+2}$ . Graphically, the quantity of lead sorbed by the soil is equal to the area between the solid and broken line in Figure 28 .

Columns of each soil 10 cm in length were also leached with quantities of 100 ppm  $\text{PbCl}_2$  that were sufficient to saturate the top 2 or 3 cm of soil with Pb. Soils were then sliced into 1 cm sections and the total Pb content of each section was determined (Figure 29). The value obtained for the surface cm was compared with its sorption capacity obtained by other methods. Values obtained by the three different methods were comparable. Values presented in Tables 23 and 24 are from isotherms. Figures 30-36 are from leaching experiments.

Lead concentration in isotherm solutions and column effluents was determined by atomic absorption after acidifying the solutions. Lead in the soil sections was extracted in 1 N HCl and determined by atomic adsorption.

### 3. Results and Discussion

The effect of increasing C.E.C., organic matter content and total surface area can be seen by comparing leaching

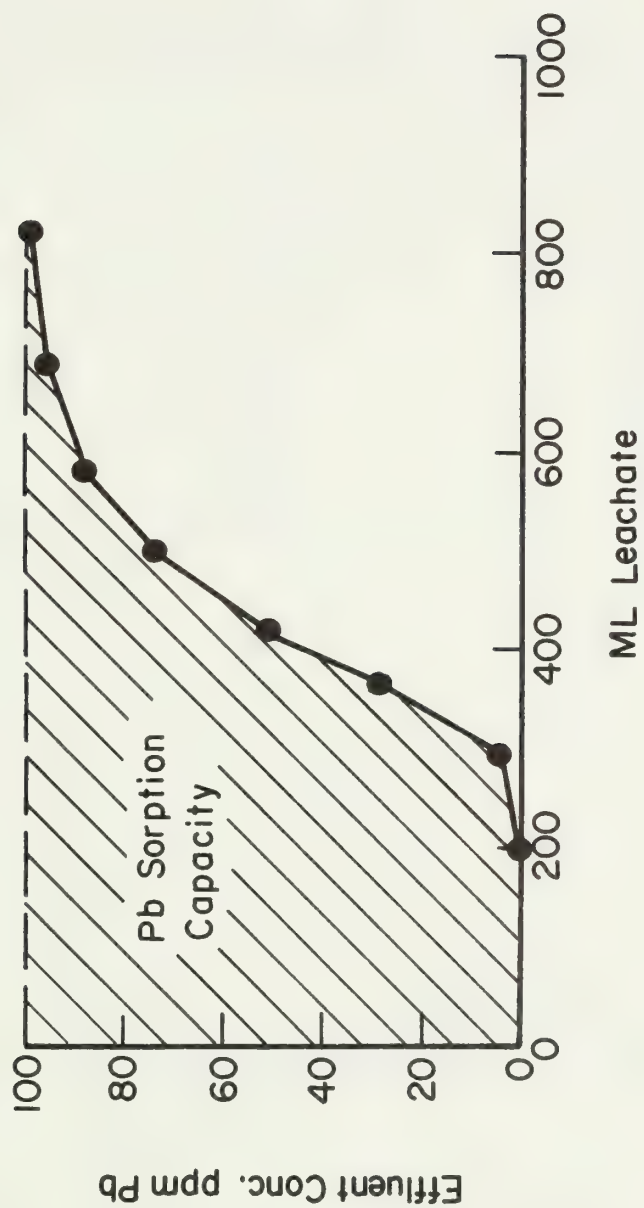


Figure 28  
Idealized Leaching Curve

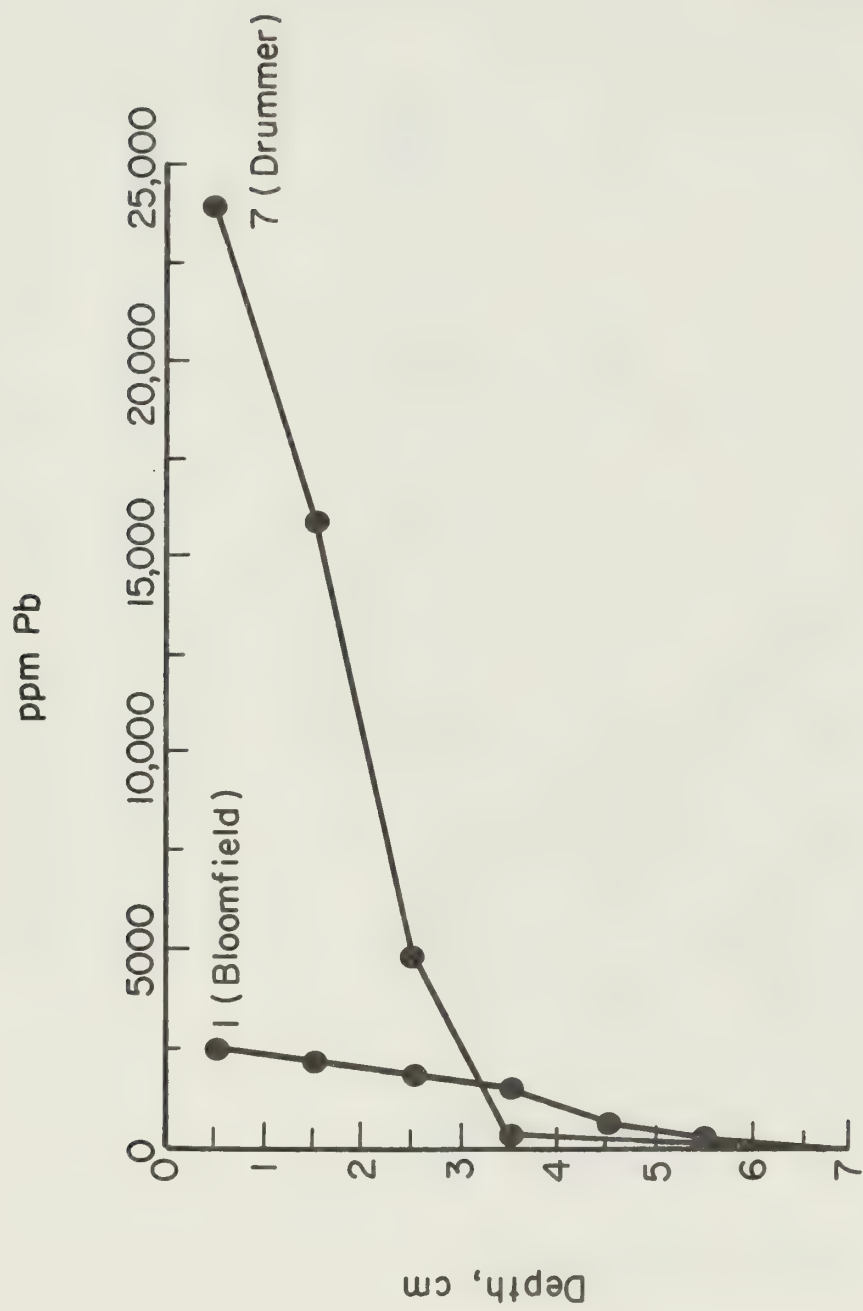


Figure 29  
Lead Leaching Profile of Soil 7 (Drummer) and Soil 1  
(Bloomfield)

Table 24

## Pb Sorption Capacity of Selected Illinois Soils

<u>Soil</u>	<u>Pb (<math>\mu</math>g Pb/g soil)</u>	<u>Pb (m mole Pb/g soil)</u>
1. Bloomfield	2,300	9.68
2. Cisne	2,894	13.97
3. Cisne	9,258	44.6
4. Cisne	6,115	29.5
5. Flanagan	19,900	96.4
6. Sidell	15,250	73.5
7. Drummer	24,350	117.5

curves for soils 1, 4, 5, and 7 in Figure 30 . This shows a dramatic increase in Pb sorption, from 2,300  $\mu\text{g}$  Pb/g soil for Bloomfield loamy sand to 24,350  $\mu\text{g}$  Pb/g for Drummer silty clay loam.

The effect of soluble P is shown in Figure 31 . Soils 4 and 3 are Cisne soils from the Toledo research field. These soils have approximately the same pH, C.E.C. and organic matter contents, but have been maintained at different P levels. Soil 4, which has a  $P_1$  value of 63, showed a lower sorptive capacity 6115  $\mu\text{g}$  Pb/g soil, than soil 3 which has a  $P_1$  value of 96 and had a sorptive capacity of 9258  $\mu\text{g}$  Pb/g soil. This suggests that Pb was precipitated in the soil as a phosphate.

The effect of soil pH on Pb sorption can be ascertained by comparing leaching cuves for soils 2 and 4. (Figure 32) Soils 2 and 4 are also Cisne soils from the Toledo research field that have similar cation exchange capacities, soluble P levels and organic matter contents, but they have been maintained at different pH levels. Soil 4 which has a pH of 6.3, the recommended pH for corn, soybean agriculture in Illinois, showed an increase in Pb sorption, 6115  $\mu\text{g}$  Pb/g soil over Soil 2 with a pH of 5.4 and a sorption capacity of 2894  $\mu\text{g}$  Pb/g soil. The



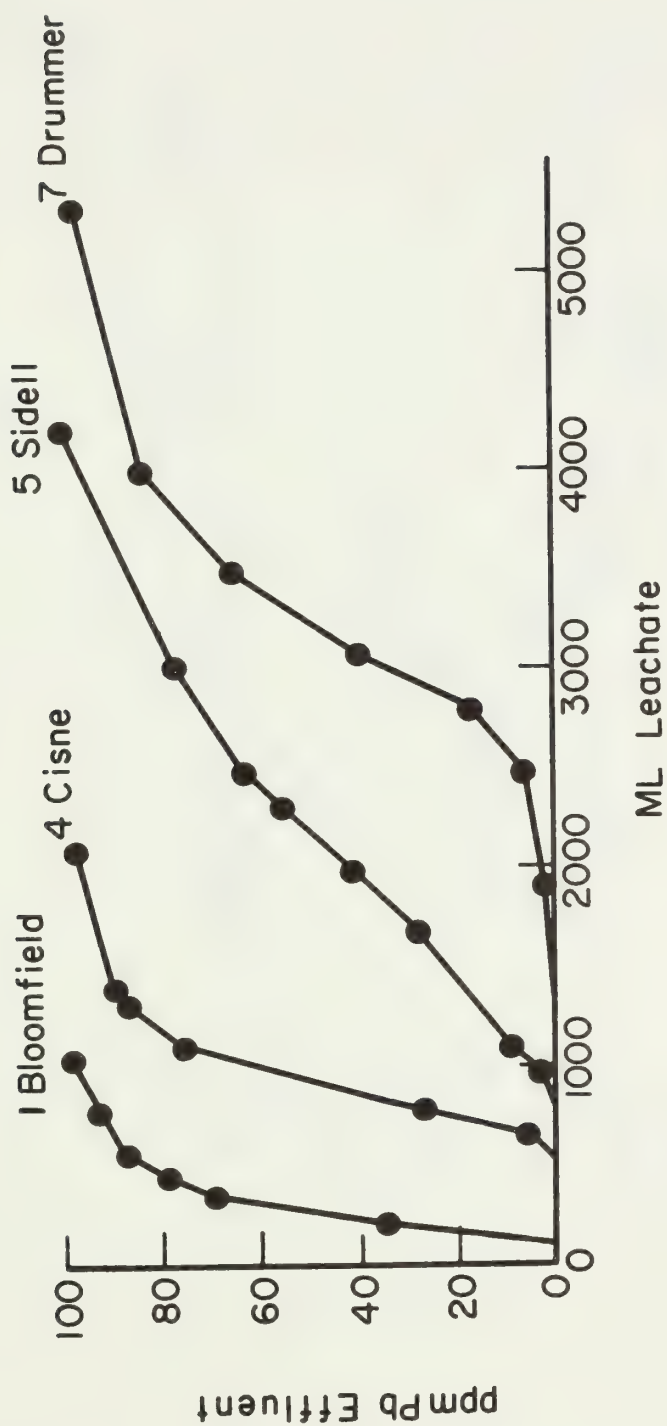


Figure 30  
Effect of Cation Exchange Capacity and Related Properties  
on Pb Sorption

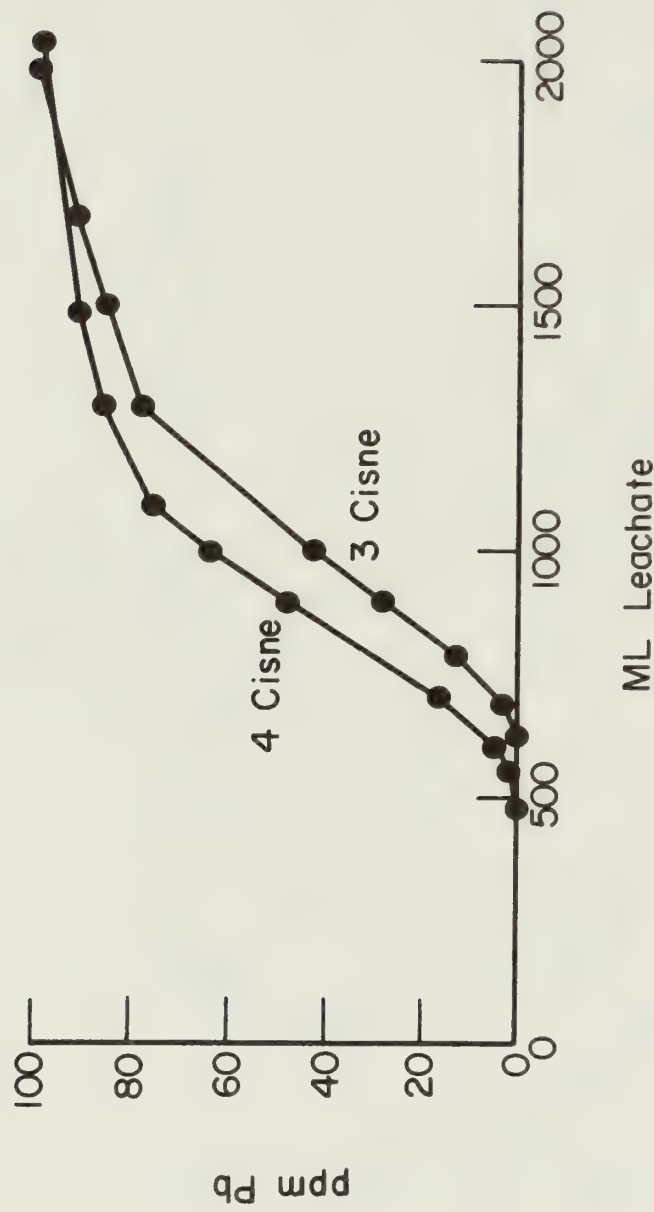


Figure 31  
Effect of Soluble P as Measured by Bray P<sub>1</sub> Test on Pb Sorption

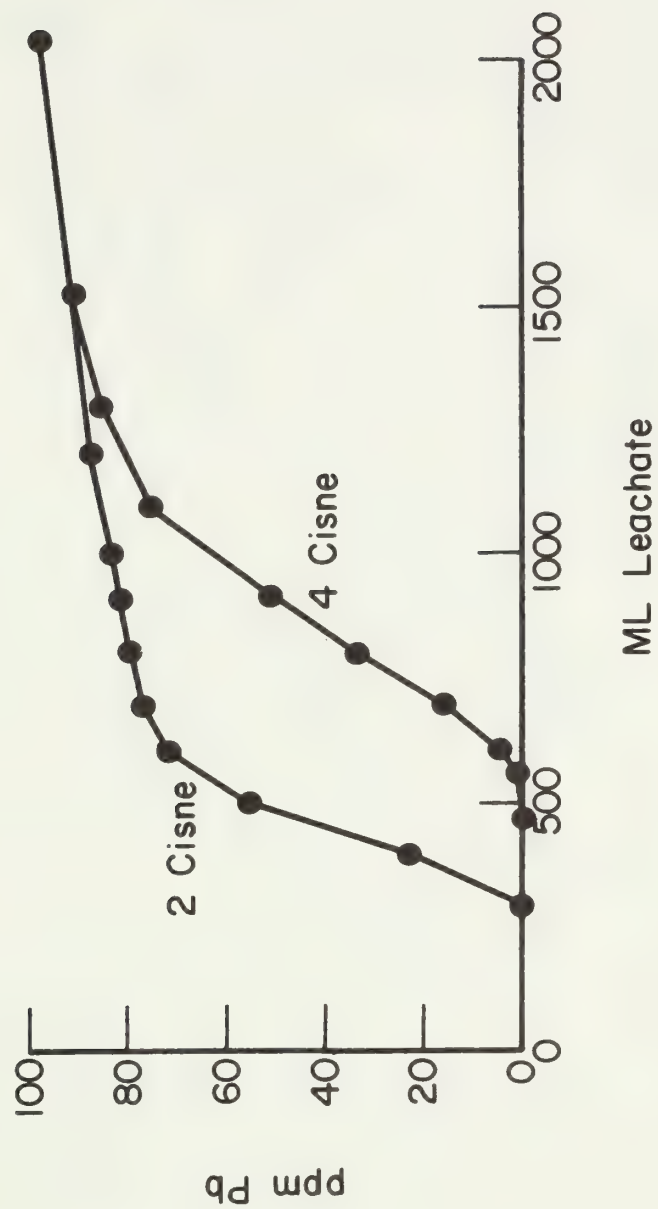
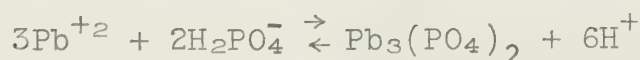
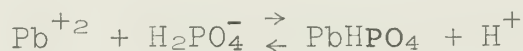


Figure 32  
The Effect of Soil pH on Pb Sorption

lower Pb sorption in acid soils could be the result of the greater solubility of Fe, Mn and Al compounds in these soils and hence greater competition for sorption sites and phosphate ions.

To illustrate the difference in Pb sorption capacity that can be encountered in a single field, Figure 33 present the leaching curves of a catena from the University of Illinois Agronomy South Farm. Soil 6, Sidell is moderately well drained, Soil 5, Flanagan is somewhat poorly drained and Soil 7, Drummer is poorly drained. These soils have formed moderately deep loess over loam textured till. Soil 7 has a silty clay loam surface while Soils 5 and 6 have silt loam surfaces. In addition, there was also an increase in C.E.C. and organic matter content with poorer drainage.

Effluent pH was monitored for the various leaching curves. Figure 34 shows the type of pH change encountered for all soils. The large change in pH associated with the sorption of Pb suggests the specific sorption of Pb by surfaces such as iron oxide in the soil and/or the precipitation of Pb as  $\text{PbHPO}_4$  or  $\text{Pb}_3(\text{PO}_4)_2$



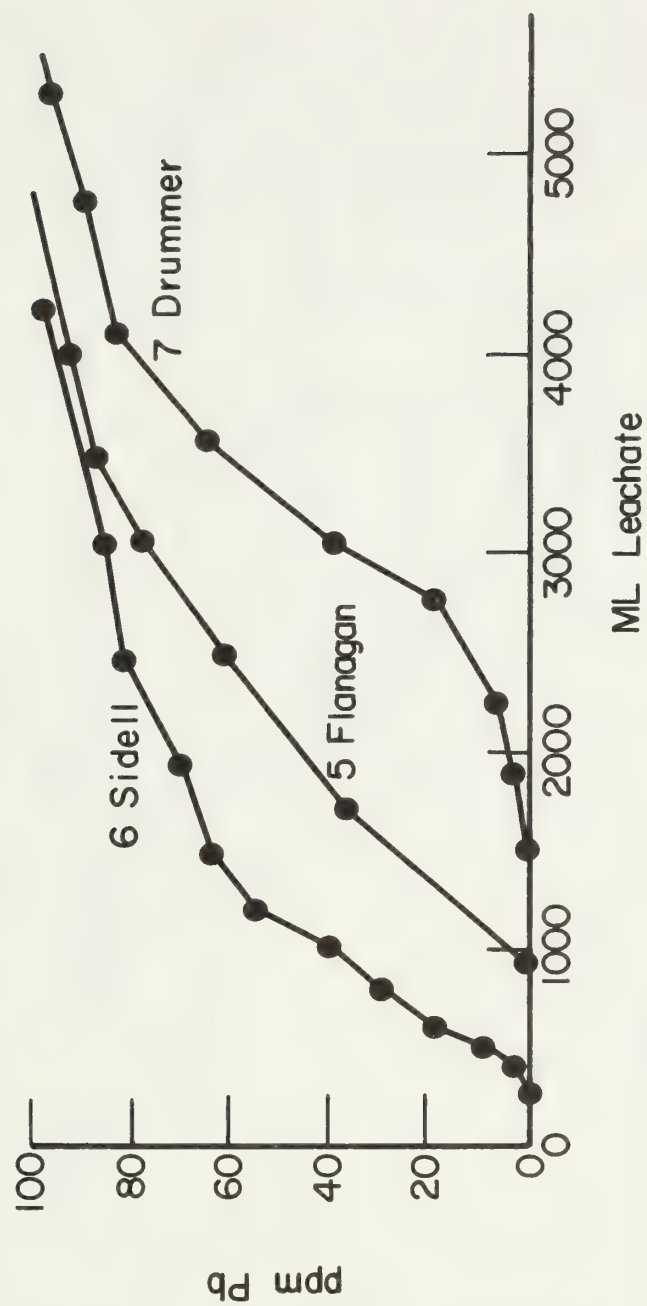


Figure 33  
Variations of Pb Sorption Capacities within a Catena

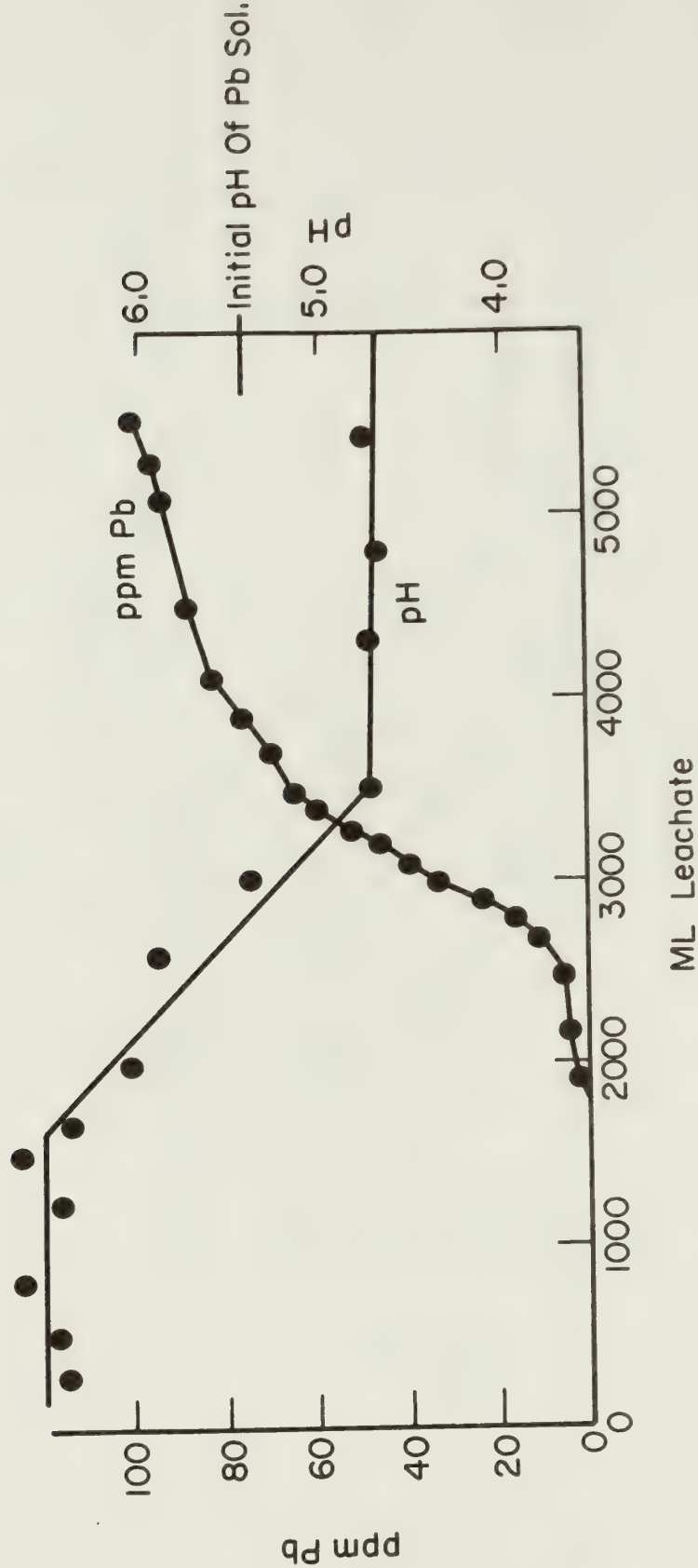


Figure 34  
pH Shifts in Drummer Soil upon Leaching with 100 ppm PbCl<sub>2</sub>



These types of pH shifts upon the addition of  $\text{PbCl}_2$  to soils were also in preliminary greenhouse experiments. In subsequent greenhouse experiments a limiting requirement for each soil and each Pb addition was calculated and the soils were ammended back to their original pH levels.

Table 24 presents a summary of the capacities of selected Illinois soils to sorb Pb. The capacity of these Illinois soils to sorb Pb was affected by texture and the texture associated properties; i.e., C.E.C., surface area, organic matter content, by soil pH and soluble P. These factors should be considered if soil is to be used in a waste disposal system where Pb is a significant effluent cation.

## 2. Leaching Studies on the Movement of High Concentrations of Pb through Soil Columns.

Figure 35 shows the leaching profiles obtained by leaching four different 10 cm long columns of Bloomfield loamy sand with 100, 200, 400, and 800 ml of 100 ppm Pb as  $\text{PbCl}_2$ .

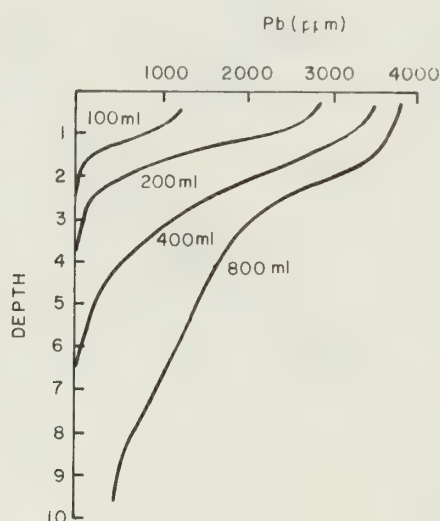


Figure 35. Leaching Profiles of Pb in Bloomfield Soil after Leaching with Variable Volumes of 100 ppm  $\text{PbCl}_2$ .

The next two figures (36 & 37) show the leaching profiles obtained by first leaching eight different 10 cm columns of Bloomfield soil first with 450 ml of 100 ppm Pb as  $\text{PbCl}_2$  then with either 0, 100, 200, 400 ml of 100 ppm Ca as  $\text{CaCl}_2$ . Figure 12 is columns that were leached with  $\text{PbCl}_2$  then dried at  $50^\circ \text{C}$  for 24 hours then leached with  $\text{CaCl}_2$ .

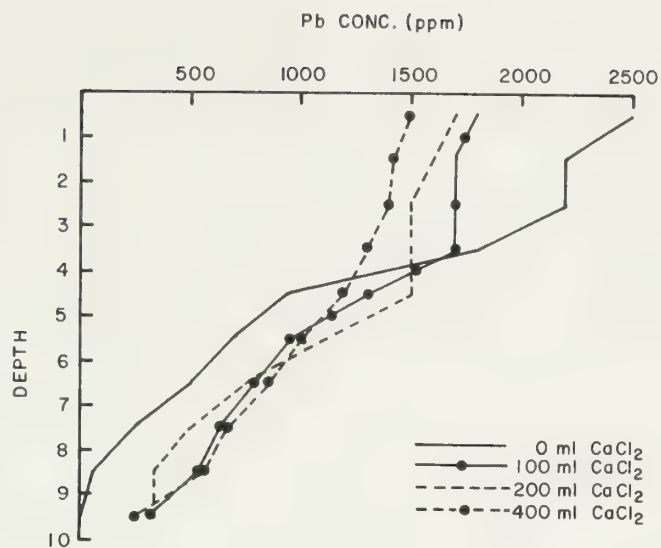


Figure 36. Movement of Pb in the Soil Profile with Varying Amounts of  $\text{CaCl}_2$ .

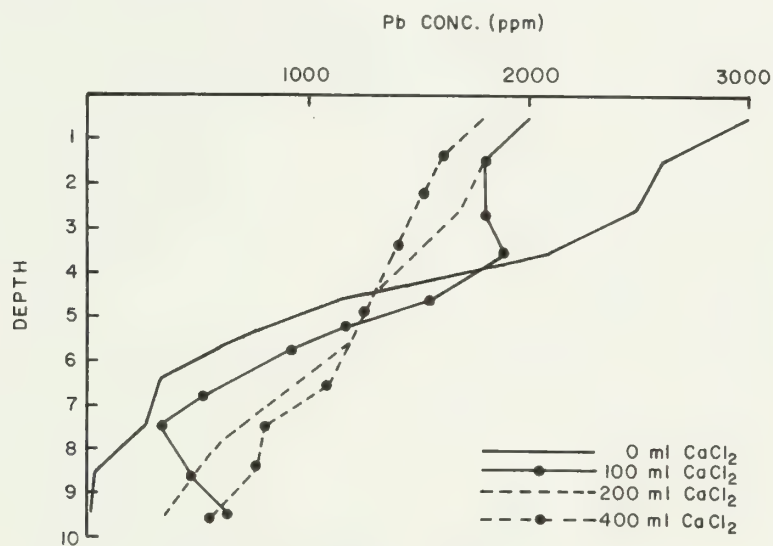


Figure 37. Movement of Pb in the Soil Profile with Varying Amounts of  $\text{CaCl}_2$ .

These results suggest that a portion of the lead sorbed by the soil can be removed by leaching with a competitive cation such as  $\text{Ca}^{++}$ . This probably represents exchangeable Pb, and the movement or loss of Pb out of these columns is dependent on the amount of nonexchangeable sites available or the amount of phosphorus available to precipitate Pb in the lower part of the column.

Figure 37 demonstrates that drying for short periods of time does not reduce the amount of leaching of Pb.

Figure 38 shows the concentration of Pb in the effluent of a 10 cm column of Bloomfield soil that was first leached with 100 ppm  $\text{PbCl}_2$  then 100 ppm  $\text{CaCl}_2$  then 1 N EDTA.

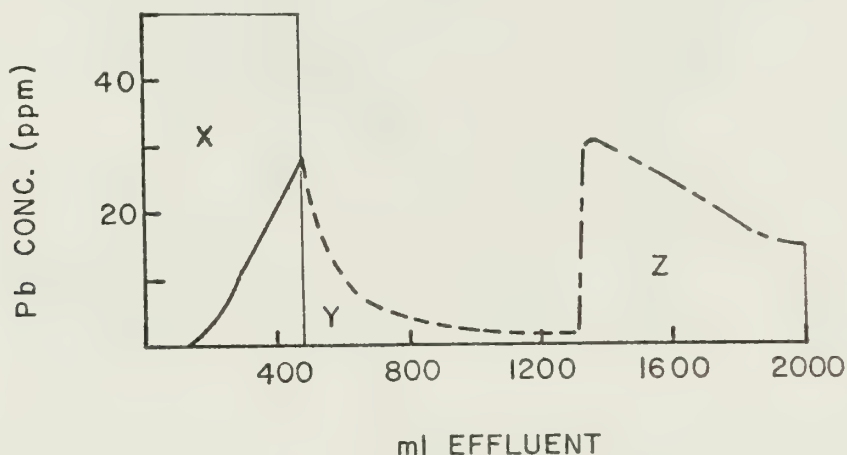


Figure 38. Concentration of Pb in Effluent from Bloomfield Soil Leaching first with  $\text{PbCl}_2$ , and finally with EDTA.

These results show that only about a third of the Pb retained in the soil (area x) can be removed by leaching with  $\text{CaCl}_2$  (area y), but most of the Pb can be removed by leaching

with EDTA (area z).

These studies suggest that high concentrations of lead, how high depends on the soil type, will move through the soil in the presence of competitive cations or complexing agents. While concentration ranges of Pb found in soils near roads (250-500 ppm) do not move in the presence of competitive cations, lead may be mobile in these soils in the presence of natural complexing agents. This possibility needs additional work.

### 3. Capacity of Selected Illinois Soils to Sorb Cd from Aqueous Solution.

Sorption isotherms for Cd on the same soils used in part one have been completed. The results are presented in Table 25. In general, soils sorb about 2.3 times less Cd than Pb on a mmole of ion per gram of soil basis. This would suggest that Cd should have a greater mobility in soils and be more available to plants.

Table 25. Sorption Capacity of Selected Illinois Soils for Cd.

<u>Soil</u>	<u>Cd(ppm/g)</u>	<u>Cd(mmole/g)</u>
1. Bloomfield	590	5.25
2. Cisne	605	5.38
3. Cisne	2000	17.79
4. Cisne	1400	12.45
5. Flanagan	4200	34.3
6. Sidell	3900	34.6
7. Drummer	4700	41.8

Cd sorption increases with increasing CEC and increasing pH as Pb sorption did, but it does not increase with increasing phosphorus levels as Pb did. This can be explained by comparing the solubility products of Pb vs Cd phosphate. Cd phosphate has a higher solubility than Pb phosphates.



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#### 4. Lead, Cadmium, and Calcium Selectivity Coefficients on a Montmorillonite, Illite, and Kaolinite

##### Background

The recognition of potential health hazards associated with lead, cadmium, and other heavy metals entering the food chain has brought attention to the levels of these metals in plants and soils, Patterson, 1965; Schroeder, 1965. Many reports have also described inhibition of plant growth by lead and cadmium, Haghiri, 1973; John et al., 1972; Miller and Koeppe, 1970; Page et al., 1972. Consequently, much attention has been focused on the ability of plants to take up trace metals from the soil and translocate them to upper plant parts, Baumhardt and Welch, 1972; Lagerwerff, 1971.

That lead, cadmium and other trace metals tend to accumulate in soils is well established. Increased levels of lead and cadmium have been reported adjacent to roadways with the concentration decreasing with distance from the highway, Chow, 1970; Lagerwerff and Apecht, 1970. Leaded gasoline has been extensively discussed as a major source of lead, and the burning of diesel oil and attrition of automotive tires has been implicated in

cadmium accumulation, Lagerwerff, 1967; Lagerwerff and Apecht, 1970. Lead and cadmium impurities in agricultural chemicals may also account for some accumulation in soils, Lagerwerff and Apecht, 1970; Schuck and Locke, 1970. However, little is known about how the metals are distributed in the soil or about their movement between the soil fractions. Initial investigations have generally concentrated on the fixation or immobilization of heavy metals by soils, Dedolph et al., 1970; Zimdahl et al., 1973. It is important that we learn how the metals are distributed in the soil in order to understand and predict the availability of these metals to plant uptake and movement through the soil by leaching. To understand and predict this distribution in a complex soil one must consider the types and strengths of metal interactions with individual soil components.

This report presents exchange adsorption data for lead, cadmium and calcium on three types of clay minerals commonly found in soils. If the exchange of lead and cadmium versus calcium is known, the exchange relationships of lead and cadmium versus other common soil cations can be estimated.

## 2. Materials and Methods

Samples of Upton, Wyoming montmorillonite (A.P.I. No.

25), Beaver's Bend illite, and kaolinite<sup>1</sup> clay were chosen as representative types of clay. With montmorillonite the  $<2\mu$  and with illite the  $<50\mu$  size fractions were obtained by sedimentation according to Stoke's Law. With kaolinite the  $<2\mu$  size fraction was used as obtained from the company. Samples of clay of the above sizes were made homoionic for the appropriate cation by shaking with 1 M solutions of  $\text{CaCl}_2$ ,  $\text{CdCl}_2$  or  $\text{Pb}(\text{NO}_3)_2$ . The clays were separated by centrifuging and the procedure repeated a total of three times. Excess salts were washed from the clays until the conductance of the wash solutions was approximately  $5\mu$  Mhos (three to four washings).

The cation exchange capacity (C.E.C.) of the montmorillonite was calculated from its molecular formula (4) for Pb (100.8 meq/100 g), Cd (105.8 meq/100 g), and Ca (110.0 meq/100 g) saturated clays. The C.E.C.'s for illite (15.4 meq/100 g) and kaolinite (2.2 meq/100 g) were determined experimentally by saturation with  $\text{NH}_4^+$  and distillation of  $\text{NH}_3$  from a sodium chloride extract and

---

<sup>1</sup>Thiele Kaolin Company, Sandersville, Georgia.

and titration, Peech et al., 1947. The montmorillonite and illite clays were equilibrated with a series of solutions having a total salt concentration of 1.0 mM whereas the kaolinite was equilibrated with a series of solutions having a total salt concentration of 0.25 mM. The counterion was chloride in all cases. The clay concentration in the equilibrating solutions was 1% or less so that the quantity of available ions in solution was 2 to 3 times the clay exchange capacity.

After equilibrating a minimum of four hours the suspensions were centrifuged, the solutions decanted, and the concentrations of cations in solution determined by atomic absorption. The ratio of cations on the clay was determined from the change in original cation concentrations in the solution phase and prior knowledge of the exchange capacity of the clay suspension. (Duplicate experiments were carried out with clays saturated in each cation, to assure that the initial clay cation had no effect on the equilibrium.)

### 3. Theoretical Considerations

Several theories have been applied to the exchange of two cations between a clay surface and a dilute aqueous solution, Babcock, 1963. In the case of divalent-divalent ion pair exchange (according to the reaction



$B^{+2}\text{-clay} + A^{+2}\text{-solution} \rightarrow A^{+2}\text{-clay} + B^{+2}\text{-solution}$ ) both the mass action and statistical thermodynamic approach result in the same expression for the thermodynamic equilibrium constant, Krishnamoorthy and Overstreet, 1950. The thermodynamic equilibrium constant,  $K_B^A$ , is given by

$$K_B^A = \frac{\gamma_A(\bar{A}) \cdot \gamma_B(B)}{\gamma_B(\bar{B}) \cdot \gamma_A(A)}$$

where A and B are the concentrations of the two ions,  $\gamma_A$  and  $\gamma_B$  are the activity coefficients, and barred quantities refer to the clay surface phase. For a divalent-divalent exchange in dilute solutions of strong electrolytes, the ratio of the solution phase activity coefficients is essentially unity. From this consideration, the experimentally determined equilibrium selectivity coefficient  $K_s$  has been defined as

$$K_{sB}^A = \frac{(X_A)(B)}{(X_B)(A)}$$

where  $X_A$  and  $X_B$  are the mole fractions of the two ions adsorbed on the clay surface. If there are no interactions between adsorbed ions and all exchange sites are alike,  $K_s$  will have a constant value independent of surface composition. In such an ideal case, the surface phase



activity coefficients would have a constant value of unity so that the selectivity coefficient equals the thermodynamic equilibrium constant, Gast, 1972.

#### 4. Results and Discussion

Values of the experimentally determined selectivity coefficients,  $K_s$ , for the exchanges of  $Pb^{+2}$ ,  $Cd^{+2}$  and  $Ca^{+2}$  on montmorillonite, illite and kaolinite are given in Table 26 for varying clay surface compositions ( $X_i$ ). For comparison selectivity coefficients determined for the clays initially saturated with each of the cations are given.

Plots of  $K_s$  versus  $X_i$  are shown in Figure 39 for the exchange reactions on the three clays. In general, the selectivity coefficients did not vary in a consistent manner over the 10 to 90% range of  $Pb^{+2}$  and  $Cd^{+2}$  surface saturations. The constant  $K_s$  over this range of surface compositions may indicate that the adsorption sites were all similar and that there was little or no interaction between adsorbed ions.

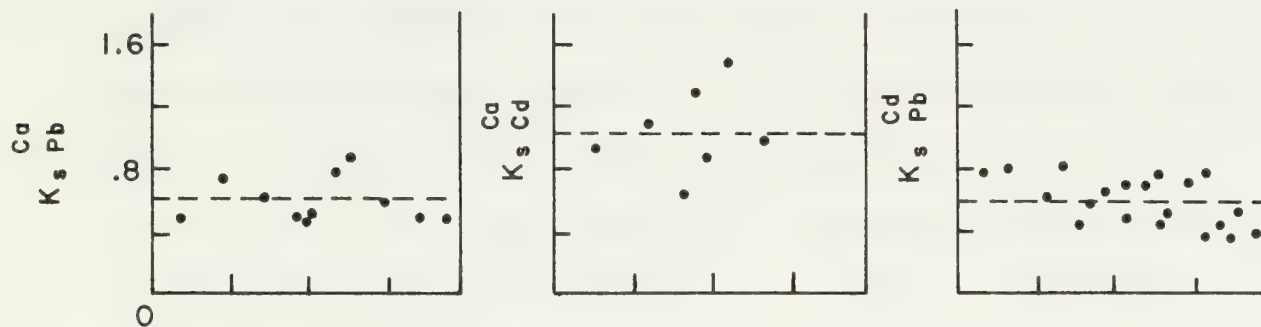
The differences in the average selectivity coefficients determined for the montmorillonite, illite and kaolinite were not great. The  $K_{SPb}^{Ca}$  values were 0.60, 0.44, and 0.34, respectively, for montmorillonite, illite, and kaolinite,

Table 26

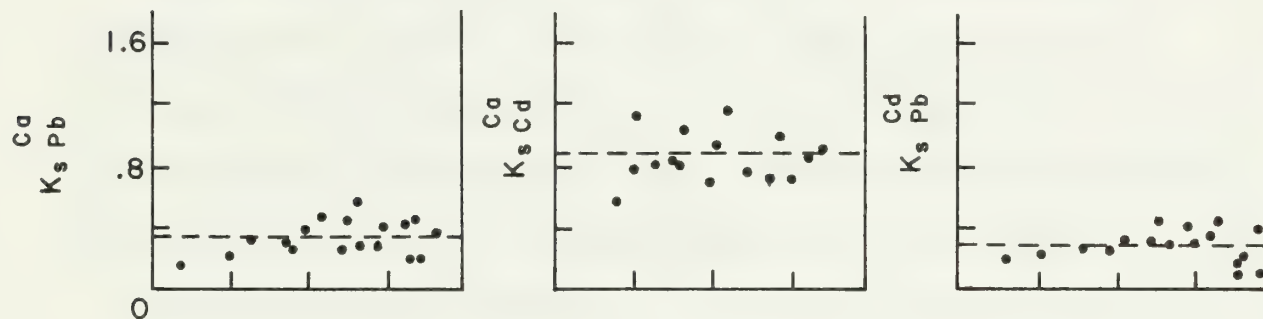
Experimentally Determined Selectivity Coefficients,  $K_s$ , at Different Mole Fractions of the Cation on the Clay,  $X_i$ , for the Exchanges of  $Pb^{+2}$ ,  $Ca^{+2}$  and  $Cd^{+2}$  on Montmorillonite, Illite, and Kaolinite

Initial Clay Saturation	Montmorillonite				Illite				Kaolinite			
	$X_{Pb}$	$K_{spb}^{Ca}$	$X_{Cd}$	$K_{sCd}^{Ca}$	$X_{Pb}$	$K_{spb}^{Ca}$	$X_{Cd}$	$K_{sCd}^{Ca}$	$X_{Pb}$	$K_{spb}^{Ca}$	$X_{Cd}$	$K_{sCd}^{Ca}$
Preferred Ion*	.96	.48	.56	1.5	.96	.25	.27	.35	.96	.64	.64	.64
	.88	.47	.45	1.3	.89	.33	.30	.35	.95	.50	.50	.50
	.75	.59	.30	1.1	.88	.43	.32	.30	.91	.48	.48	.48
	.63	.60	.14	.92	.81	.54	.73	.73	.82	.41	.41	.41
	.52	.52			.81	.34	.43	.71	.77	.41	.41	.41
	.47	.43			.63	.37	.35	.71	.74	.41	.41	.41
					.63	.37	.35	.71	.66	.35	.35	.35
					.59	.50	.53	.61	.55	.47	.47	.47
					.52	.45	.47	.61	.44	.47	.47	.47
					.50	.32	.32	.61	.38	.41	.41	.41
Non Preferred Ion	.65	.87	.87	1.00	.75	.52	.32	.41	.99	.89	.89	.89
	.60	.78	.67	.98	.69	.57	.36	.41	.81	.81	.81	.81
	.51	.63	.49	.88	.64	.49	.30	.41	.70	.68	.68	.68
	.37	.64	.41	.63	.60	.43	.41	.41	.71	.68	.68	.68
	.24	.56			.54	.43	.33	.41	.62	.62	.62	.62
	.11	.47			.44	.43	.37	.41	.57	.57	.57	.57
					.35	.44	.32	.41	.50	.50	.50	.50
					.29	.44	.32	.41	.47	.47	.47	.47
					.17	.34	.31	.41	.41	.41	.41	.41
					.09	.23	.30	.41	.35	.35	.35	.35
Average $K_s$		.60		1.04		.44		1.01		.38		.38

## MONTMORILLONITE



## KAOLINITE



## ILLITE

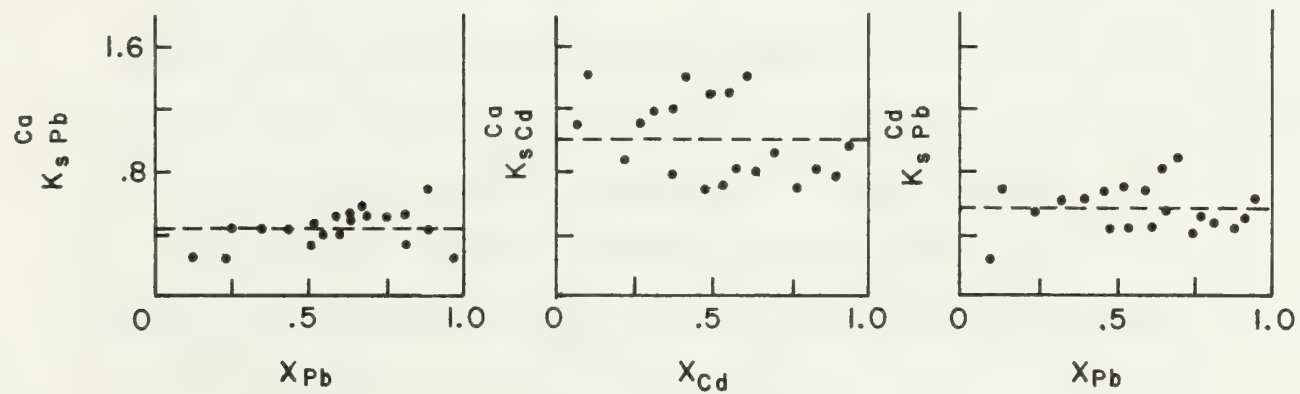


Figure 39

Plots of  $K_s$  vs  $X_i$  for Exchanges of  $Pb^{+2}$ ,  $Cd^{+2}$ , and  $Ca^{+2}$   
 on Montmorillonite, Illite, and Kaolinite

indicating that  $\text{Pb}^{+2}$  adsorption was favored over  $\text{Ca}^{+2}$  on all three clays with the most preference being for kaolinite. Little difference was found between  $\text{Ca}^{+2}$  and  $\text{Cd}^{+2}$  exchange as indicated by  $K_{\text{SCd}}^{\text{Ca}}$  values near unity, i.e., 1.04, 1.01, and 0.89, respectively, for montmorillonite, illite and kaolinite. Since there was little difference in selection between  $\text{Ca}^{+2}$  and  $\text{Cd}^{+2}$  on the clays, one would expect that the values of  $K_{\text{SPb}}^{\text{Cd}}$  would be very similar to those of  $K_{\text{SPb}}^{\text{Ca}}$ . Indeed the experimentally determined  $K_{\text{SPb}}^{\text{Cd}}$ , 0.58, 0.56, and 0.31, respectively, for montmorillonite, illite and kaolinite, compare quite favorably with  $K_{\text{SPb}}^{\text{Ca}}$ .

These results indicate that  $\text{Pb}^{+2}$  and  $\text{Cd}^{+2}$  may compete with common divalent ions in the soil such as  $\text{Ca}^{+2}$  for clay adsorption sites. Whereas, although  $\text{Cd}^{+2}$  competes more or less on an even basis with  $\text{Ca}^{+2}$  for clay adsorption sites, the adsorption of  $\text{Pb}^{+2}$  is favored by a factor of 2 or 3 over  $\text{Ca}^{+2}$ . Suggesting that there may be relatively more  $\text{Cd}^{+2}$  in a soil solution and thus be available to plants. Some  $\text{Cd}^{+2}$  uptake is related at least partially to solution concentration, Page et al., 1972, this implies that ions may not bind up as much  $\text{Cd}^{+2}$  as  $\text{Pb}^{+2}$ .

The exchange behavior of  $\text{Pb}^{+2}$  and  $\text{Cd}^{+2}$  vs  $\text{Ca}^{+2}$  on several soils with varying clay mineral fractions has been

reported by Lagerwerff and Brower, 1972 and 1973. Their results show that  $Pb^{+2}$  adsorption to soils is favored over  $Ca^{+2}$  adsorption as the results with pure clays would predict. Contrary to the results with pure clays,  $Ca^{+2}$  adsorption to soils was found to be significantly favored over  $Cd^{+2}$  adsorption, Lagerwerff and Brower, 1972. Since their Cd-Ca exchange data for soils were obtained over a range of only .14 to 1.6%  $Cd^{+2}$  saturation of the soil exchange capacity, the results may not be comparable to the pure clay data where  $Cd^{+2}$  saturation varied from 7 to 94%.

The exchange adsorption of  $Cd^{+2}$  vs.  $Ca^{+2}$  at low  $Cd^{+2}$  saturation on Clay Spur Montmorillonite, Fithian Illite, and Birch Pit Kaolinite has been reported, Oak Ridge National Laboratory, 1973. Selectivity coefficients,  $K_{sCd}^{Ca}$ , are reported to be dependent on pH with  $Cd^{+2}$  adsorption being more favored at higher pH's. For the pH range of the experiments reported here, approximately 5 to 6, it was found that  $Ca^{+2}$  adsorption was slightly favored on the montmorillonite, that  $Cd^{+2}$  adsorption was favored on the illite and to a lesser extent on the kaolinite. This corresponds fairly well with the data reported in this study except for the results with illite. The difference in the results with illite may represent the differences between two types of illite, or it may indicate a preference for  $Cd^{+2}$  at low levels of  $Cd^{+2}$  loading on the illite.



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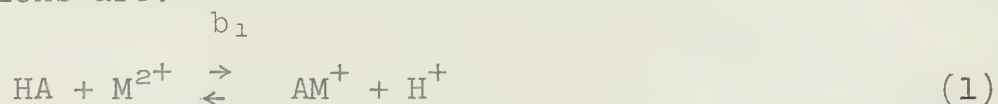
## 5. Stability (Formation) Constants of Metal-Soil Organic Matter Complexes

### Background

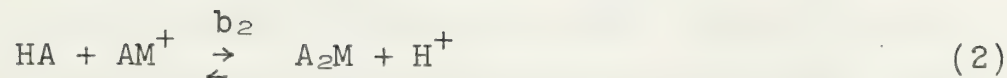
The ability of soil organic matter to form stable complexes with  $\text{Pb}^{2+}$  and other heavy metals has been well established, Stevenson and Ardakani, 1972. The compounds mainly involved are the humic and fulvic acids, which can best be described as a series of yellow- and black-colored polyelectrolytes having an unusually high content of acidic functional groups. Formation constants are required for an understanding of the role of these constituents in transport processes and in the uptake of  $\text{Pb}^{2+}$  by plants, microorganisms, and faunal organisms.

### 2. Procedures

The potentiometric method as applied to synthetic polyelectrolytes was used for determining formation constants. In this case, complex formation is regarded as a competitive reaction between the metal ion and  $\text{H}^+$  for reactive sites on the ligand. For a two-step process, the reactions are:



and



where the successive constants,  $b_1$  and  $b_2$ , are given by:

$$b_1 = \frac{(\text{AM}^+)(\text{H}^+)}{(\text{HA})(\text{M}^{2+})} \quad (3)$$

$$b_2 = \frac{(\text{A}_2\text{M})(\text{H}^+)}{(\text{HA})(\text{AM}^+)} \quad (4)$$

The overall constant,  $B_2$ , is given by:

$$B_2 = b_1 b_2 = \frac{(\text{A}_2\text{M})(\text{H}^+)^2}{(\text{HA})^2(\text{M}^{2+})} \quad (5)$$

Essentially, the potentiometric method requires calculations for two main functions:  $(\text{A}^-)$ , the concentration of free chelating species, and  $\bar{n}$ , the average number of ligand molecules per metal ion. The latter, referred to as Bjerrum's formation function, is given by:

$$\bar{n} = \frac{(\text{A}_t) - (\text{HA}) - (\text{A}^-)}{(\text{M}_t)} \quad (6)$$

where  $\text{M}_t$  is the concentration of metal ion. The formation function,  $\bar{n}$ , can also be defined as the ratio of  $\text{M}^{+n}$  in the complex to total metal ion concentration.

(a) Graphical Approach - The initial work was done using Bjerrum's approach as modified by Gregor et al., 1955. Titration curves were obtained for the humic acid in the absence and presence of variable amounts of metal ion, following which the concentration of undissociated functional groups, HA, was calculated using the equation:

$$(HA) = (A_t)(1-\alpha) - (H^+) \quad (7)$$

where  $(A_t)$  refers to total acidity or normality and  $H^+$  the hydrogen ion concentration at a particular value of  $\alpha$ .

The concentration of dissociated functional groups,  $(A^-)$ , was obtained by iterative solution of the equation Gregor et al., 1955:

$$K_a = \frac{(H^+)(A^-)}{(HA)} \left[ \frac{(A^-)}{(A_t) - (A^-)} \right]^{n-1} \quad (8)$$

where  $K_a$  and  $n$  were obtained by application of the modified Henderson-Hasselbalch equation:

$$pH = pK_a - n \log \frac{1-\delta}{\delta} \quad (9)$$

Solution of equation (8) was done using University of Illinois IBM 360/75 computer (Fortran IV language).

Formation curves were prepared from plots of  $\bar{n}$  vs.  $p(HA/H^+)$ , from which  $b$  was obtained at half integer values of  $\bar{n}$ .

(b) Mathematical Calculations from Basic Equation -  
Computer programs were developed based on the fundamental equation relating successive formation constants ( $B_n$ ) to  $\bar{n}$ .

$$\sum_{n=0}^{\bar{n}} (\bar{n} - n) B_n (A^-)^n = 0 \quad (10)$$

where  $(A^-)$  is the concentration of dissociated ligand.

Modification of equation (10) was required for the soil polyelectrolytes, as follows:

$$\sum_{n=0}^{\bar{n}} (\bar{n} - n) B_n (HA/H^+)^n = 0 \quad (11)$$

where HA is the concentration of undissociated ligand.

In the case of the bidentate complexes ( $Pb^{2+}$ , etc.) the desired constants were obtained by computer analysis of the following equation, using the method of least squares.

$$\frac{\bar{n}}{(\bar{n}-1)(HA/H^+)} = \frac{(2-\bar{n})(HA/H^+)}{(\bar{n}-1)} B_2 - b_1 \quad (12)$$

where  $b_1$  is the formation constant for the 1:1 complex and  $B_2 = b_1 b_2$ . Equation (12) is the expanded form of equation (11).



Results obtained for  $\text{Cr}^{3+}$  indicated that little, if any, of the 1:1 complex was formed. Accordingly,  $b_1$  was eliminated after expansion of equation (11), and a computer program was derived for calculating  $B_2(b_1b_2)$  and  $B_3(b_1b_2b_3)$  from the following relationship:

$$\frac{\bar{n}}{(\bar{n}-2)(\text{HA}/\text{H}^+)^2} = \frac{(3-\bar{n})(\text{HA}/\text{H}^+)}{(\bar{n}-2)} B_3 - B_2 \quad (13)$$

(c) Metal Titrations - Revisions were made in the potentiometric titration method in order to ascertain pH effects and to determine metal binding capacity. The basis for the calculations are given in detail below.

In the absence of metal ions, the following relationships are valid, where  $K_i$  is the ionization constant of the humic acid at any given pH, (KOH) is the amount of base consumed during titration, and the other symbols are those defined earlier.

$$A_t = (\text{HA}) + (\text{KOH}) + (\text{H}^+) - (\text{OH}) \quad (14)$$

$$A^- = (\text{KOH}) + (\text{H}^+) - (\text{OH}) \quad (15)$$

$$K_i = \frac{(A^-)(\text{H}^+)}{(\text{HA})} \quad (16)$$

The conservation equation following addition of a



divalent metal ion ( $M^{+2}$ ) is:

$$A_t = (HA) + (A^-) + (MA^+) + 2(MA_2) \quad (17)$$

The quantity  $(MA^+ + 2MA_2)$  is obtained by titration of the hydrogen liberated by addition of the metal ion (pH returned to initial starting point).

$$T = (HA) + (A^-) = A_t - (MA^+ + 2MA_2) \quad (18)$$

The assumption is subsequently made that the occurrence of chelation does not alter the dissociation relationship of the humic acid. Thus, by substituting  $(A^-)$  from equation (18) into equation (16), the following is obtained:

$$K_i = \frac{[T - (HA)] (H^+)}{(HA)} \quad (19)$$

from which HA is given by

$$(HA) = \frac{T(H^+)}{K_i + (H^+)} \quad (20)$$

The above values permit calculations to be made for  $(HA/H^+)$  and  $\bar{n}$ , which are required for the determination of formation constants according to equation (10).

A computer program was prepared for calculating  $(HA/H^+)$  and  $\bar{n}$  from the primary data.

### 3. Materials and Methods

The humic acids were obtained from four diverse sources, including peat (Terric Medhidemist), Sable silt loam (Aquic Argudoll), Harpster silt loam (Calcic Argaquoll), and a weathered North Dakota lignite (Leonardite humic acid).

Titrationes were performed with CO<sub>2</sub>-free KOH (0.1530 N) using a Beckman Model G pH meter. The usual precautions were observed to avoid uptake of atmospheric CO<sub>2</sub> during the titrations. In a typical experiment, a 20 to 30 ml sample of humic acid solution, estimated to contain from 0.08 to 0.12 me of titratable hydrogens, was added to give the desired ionic strength, and the volume was adjusted to 50 ml. Corrections were made for volume changes in calculating the final results. The metals were added as their chloride salts from carefully prepared 0.02 M stock solutions.

### 4. Results and Discussion

(a) Determination of formation constants by Bjerrum's approach as modified by Gregor et al., 1955.

The peat humic acid was used for this study and formation constants were obtained at ionic strengths ( $\mu$ ) of 0.1 and 0.01.

Titration curves of the peat humic acid ( $\mu = 0.1$ ) in the presence and absence of variable amounts of  $\text{Pb}^{2+}$  are presented in Figure 40. The appropriate Henderson-Hasselbalch plots ( $\text{pH}$  vs  $\log (1-\alpha/\alpha)$ ) are given in Figure 41. Addition of  $\text{Pb}^{2+}$  resulted in a drop in  $\text{pH}$ , the magnitude being proportional to the amount of  $\text{Pb}$  applied. The break in the curve for the high level of  $\text{Pb}^{2+}$  (shown by the arrow) is due to formation of the basic salt, as indicated by blank titrations of  $\text{Pb}^{2+}$ . In the presence of  $\text{Pb}^{2+}$ , the plots were depressed downward and showed pronounced curvature, suggesting the formation of rather stable complexes, Gregor et al., 1955. Similar results were obtained at  $\mu = 0.01$  except that the  $\text{pH}$  drop was greater.

The main effect of ionic strength on the humic acid (no metal additions) was parallel displacement of the curves, which suggests that the  $\text{COOH}$  groups are not alike. Values for  $\text{pK}_a$  and  $n$  by application of the Henderson-Hasselbalch equation are as follows:

<u>Ionic Strength (<math>\mu</math>)</u>	<u><math>\text{pK}_a</math></u>	<u><math>n</math></u>
0.01	4.93	1.90
0.10	4.77	1.82

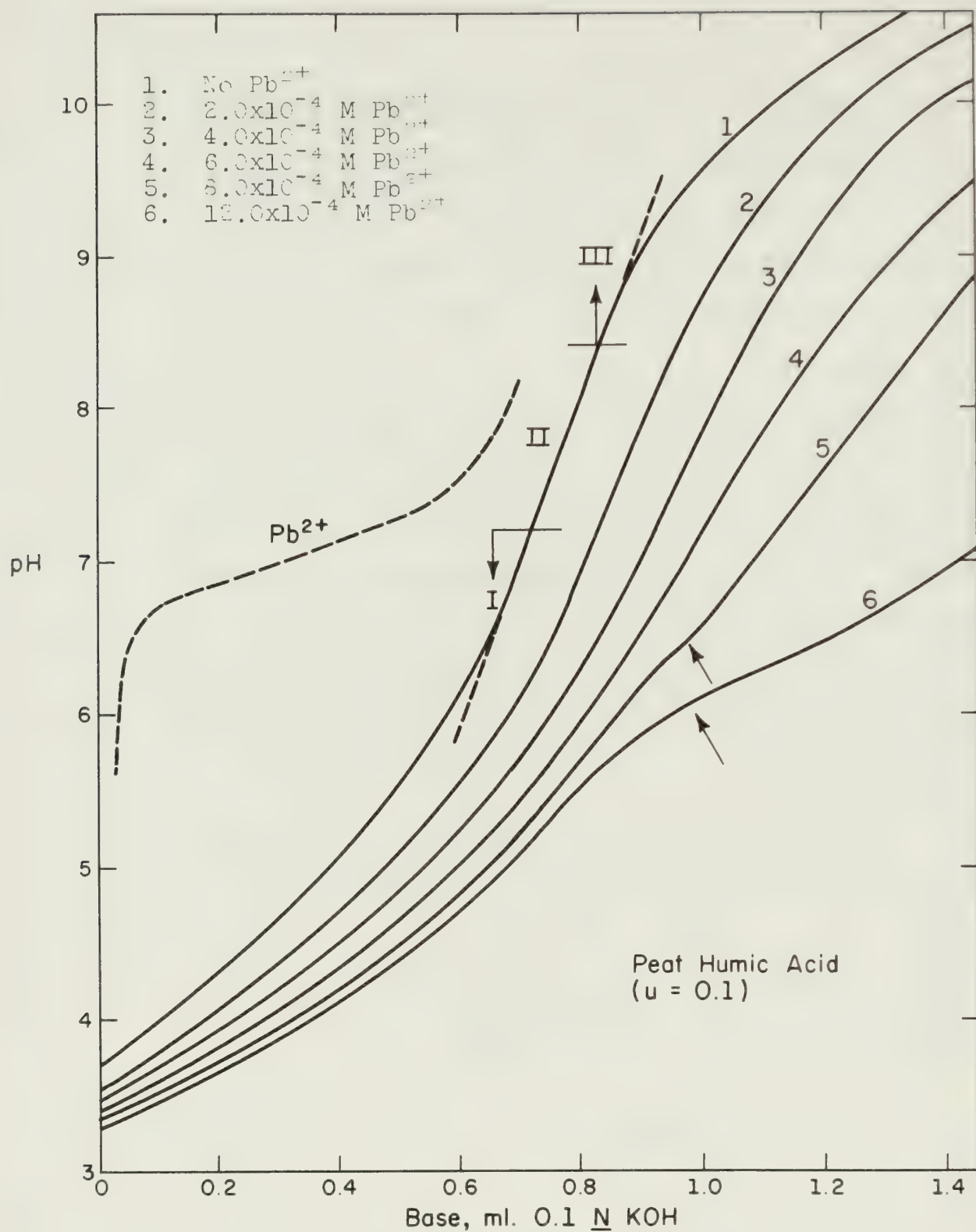


Figure 40

Titration Curves of Peat Humic Acid in the Presence of Variable Amounts of  $\text{Pb}^{2+}$ . The Arrow Denotes Formation of the Basic Salt.

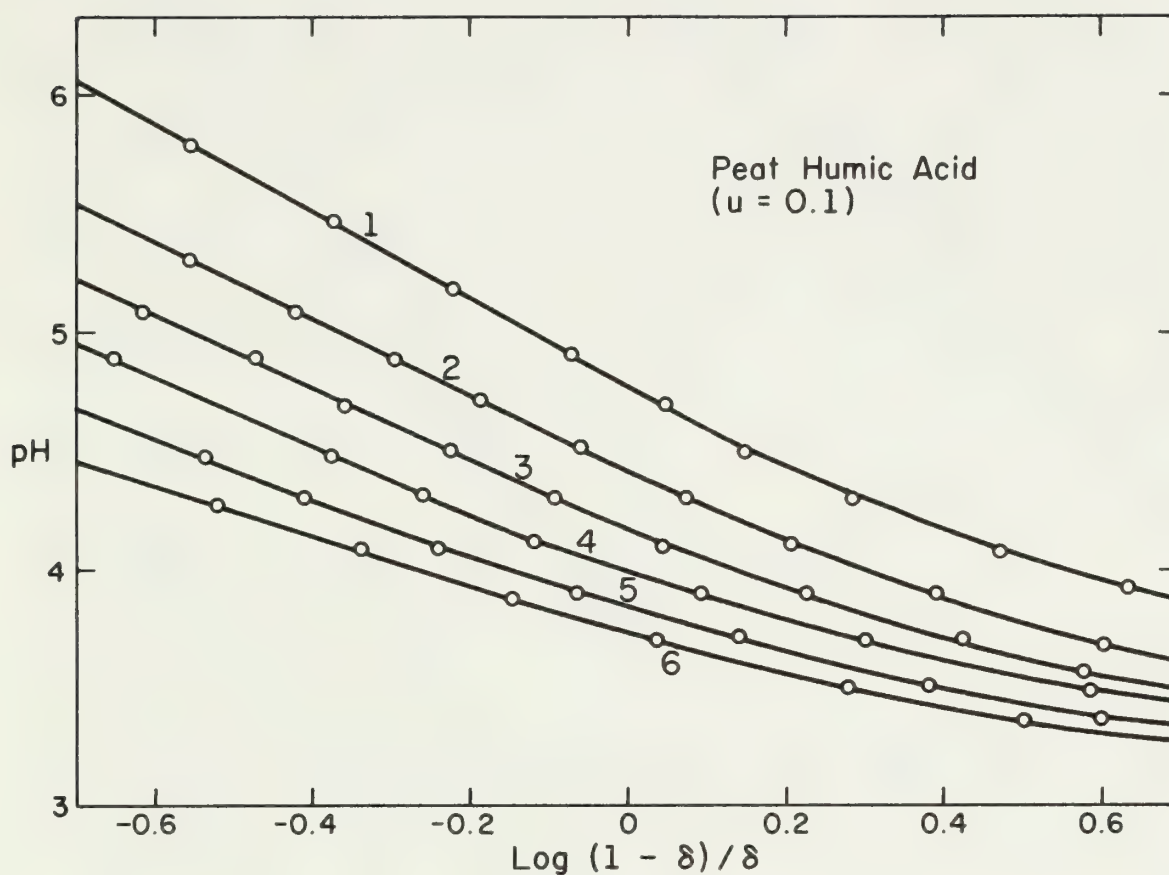


Figure 41

pH vs. Log  $(1 - \delta) / \delta$  Plots of Peat Humic Acid in the Presence  
of Variable Amounts of  $\text{Pb}^{2+}$

1. No  $\text{Pb}^{2+}$
2.  $2.0 \times 10^{-4}$  M  $\text{Pb}^{2+}$
3.  $4.0 \times 10^{-4}$  M  $\text{Pb}^{2+}$
4.  $6.0 \times 10^{-4}$  M  $\text{Pb}^{2+}$
5.  $8.0 \times 10^{-4}$  M  $\text{Pb}^{2+}$
6.  $12.0 \times 10^{-4}$  M  $\text{Pb}^{2+}$

It is noteworthy that horizontal displacement of the titration curves occurred at all levels of  $\text{Pb}^{2+}$  addition, which could have been due to basic salt formation at the higher pH's but more likely to dissociation of bound water from covalently linked Pb (1:1 complexes) or release of  $\text{H}^+$  from an otherwise nontitratable weak acid group of the humic acid. Errors introduced into the calculations of  $\bar{n}$  and  $\text{p}(\text{HA}/\text{H}^+)$  as a result of possible hydrolysis of  $\text{Pb}^{2+}$  were taken into account in estimating "b" values from the formation curves.

Another difficulty that was encountered in using the approach of Gregor et al., 1955 is that the titration results for the humic acid in the absence of metal ions did not fit exactly the Henderson-Hasselbalch equation, particularly in the acid region. Experiments currently underway show two and possibly three slight inflections on the titration curve, indicating the presence of COOH groups with different but overlapping  $\text{pK}_a$ 's.

Formation plots ( $\bar{n}$  vs.  $\text{p}(\text{HA}/\text{H}^+)$ ) for the Pb-humic acid complexes are given in Figure 42. The curves exhibit a slight change in slope near  $\bar{n} = 0.5$ ; in general, the findings suggest that 2:1 complexes are formed simultaneously to the 1:1 complexes, and that a reading of



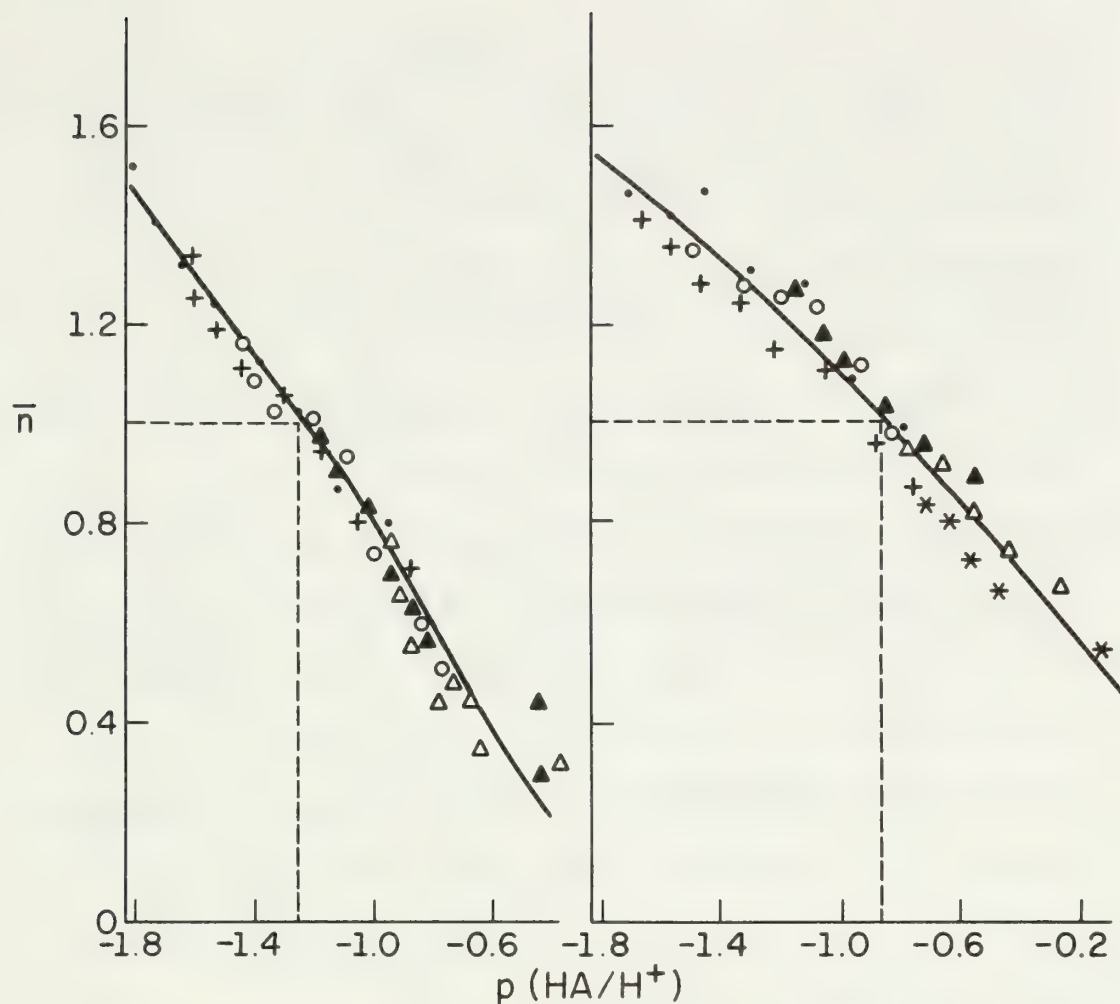


Figure 42

## Formation Plots for Peat Humic Acid

- A. Ionic Strength of 0.1: ( $\bullet$ )  $2 \times 10^{-4}$  M  $\text{Pb}^{2+}$ ; (+)  $4 \times 10^{-4}$  M; ( $\circ$ )  $6 \times 10^{-4}$  M; ( $\blacktriangle$ )  $8 \times 10^{-4}$  M; ( $\triangle$ )  $12 \times 10^{-4}$  M
- B. Ionic Strength of 0.01: ( $\bullet$ )  $1.8 \times 10^{-4}$  M; (+)  $3.6 \times 10^{-4}$  M; ( $\circ$ )  $5.4 \times 10^{-4}$  M; ( $\blacktriangle$ )  $7.2 \times 10^{-4}$  M; ( $\triangle$ )  $10.7 \times 10^{-4}$  M; (\*)  $12.0 \times 10^{-4}$  M

$p(\text{HA}/\text{H}^+)$  at  $\bar{n} = 1$  provides a meaningful expression of the average constant for the system ( $b_{\text{ave}}$ ). The overall formation constant was subsequently calculated from the relationship  $B_2 = B_{\text{ave}}^2$ , as done by Gregory et al., 1955 for  $\text{Cu}^{2+}$  complexes of polyacrylic acid.

In Table 27, formation constants ( $B_2$ ) for the humic acid are compared with those observed for  $\text{Cu}^{2+}$  complexes using the same technique, Stevenson et al., 1973. Also included are  $B_2$  values Gregor et al., 1955 reported for the  $\text{Cu}^{2+}$  complexes of polyacrylic acid and two organic acids (acetic,  $\text{CH}_3\text{COOH}$ ; glutaric,  $\text{HOOC}(\text{CH}_2)_3\text{COOH}$ ). It can be seen that  $B_2$  values for the humic acid are of the order expected for polyacrylic acid, and that humic acids probably form stronger complexes with  $\text{Pb}^{2+}$  than many simple biochemical compounds.

The formation constant ( $B_2$ ) at  $\mu = 0.01$  was higher than at  $\mu = 0.1$ , which is an agreement with other observations indicating that stronger complexes are formed at lower ionic strengths, Stevenson and Ardakani, 1972.

(b) Determination of Formation Constants from the Basic Equation Relating  $B_n$  to  $\bar{n}$  and  $p(\text{HA}/\text{H}^+)$  - This method was applied because fewer titrations were required in order to obtain the desired constants. A second

Table 27

Formation Constants ( $B_2$ ) of  $Pb^{2+}$  and  $Cu^{2+}$  with Humic Acids,  
Polyacrylic Acid, and Some Simple Organic Acids

<u>Sample</u>	<u><math>\mu</math></u>	<u><math>\log B_{ave}</math></u>	<u><math>B_{ave}</math></u>	<u><math>B_2</math></u>	<u><math>-\log B_2</math></u>
$Pb^{2+}$ Complexes					
Peat Humic Acid	0.01	-0.87	0.135	$1.8 \times 10^{-2}$	1.74
Peat Humic Acid	0.10	-1.25	0.056	$3.2 \times 10^{-3}$	2.50
$Cu^{2+}$ Complexes					
Peat Humic Acid	0.10	-1.28	0.052	$2.8 \times 10^{-3}$	2.55
Sable Humic Acid	0.10	-1.05	0.089	$7.9 \times 10^{-3}$	2.10
Polyacrylic Acid*	0.20	-1.17	0.068	$4.6 \times 10^{-3}$	2.34
Glutanic Acid*	0.20	-2.80	0.0016	$2.5 \times 10^{-6}$	5.60
Acetic Acid*	0.20	-3.09	0.0008	$6.6 \times 10^{-7}$	6.18

\*From Gregor et al, 1955. The supporting electrolyte was  
0.2 M  $NaNO_3$

modification was that individual pK's at selected pH values were used for calculating ( $A^-$ ) since the humic acids did not obey precisely the modified Henderson-Hasselbalch equation. These were secured from pH vs pK plots, where pK was calculated from the relationship  $pK = pH + \log (1-\partial/\partial)$ . Titrations were performed as before but with only two levels of metal ion additions. Experiments were carried out with  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Cu^{2+}$  at ionic strengths ( $\mu$ ) of 0.1, 0.01, and 0.001. A few experiments were also carried out with  $Cr^{3+}$ . The samples used in these experiments were the Harpster and Leonardite humic acids.

Formation constants ( $B_2$ ) for the  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Cu^{2+}$  complexes are recorded in Table 28. Stability of the complexes increased with decreasing ionic strength and followed the order:



The results of the study confirmed the conclusion arrived at earlier that 2:1 complexes were formed simultaneously to the 1:1 complexes. This was indicated by the computer printouts and also by calculating  $B_2$  by a shortened version of equation (12).

One of the objectives of the study was to ascertain if formation constants differed for humic acids from diverse

Table 28

Formation Constants ( $B_2$ ) of  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  Complexes  
with Several Humic Acids

$M^{2+}$	Ionic Strength					
	0.1		0.01		0.001	
	$B_2$	$-\log B_2$	$B_2$	$-\log B_2$	$B_2$	$-\log B_2$
Harpster Humic Acid						
$Cu^{2+}$	$2.95 \times 10^{-3}$	2.53	$4.79 \times 10^{-3}$	2.32	$5.75 \times 10^{-3}$	2.24
$Pb^{2+}$	$2.45 \times 10^{-3}$	2.61	$3.98 \times 10^{-3}$	2.40	$5.01 \times 10^{-3}$	2.30
$Cd^{2+}$	$4.90 \times 10^{-4}$	3.31	$1.32 \times 10^{-3}$	2.88	$2.19 \times 10^{-3}$	2.66
Peat Humic Acid						
$Pb^{2+}$	$3.2 \times 10^{-3}$	2.50	$1.8 \times 10^{-2}$	1.74	-	-
Leonardite Humic Acid						
$Pb^{2+}$	$2.51 \times 10^{-3}$	2.60	$7.94 \times 10^{-3}$	2.10	$1.41 \times 10^{-2}$	1.85
$Cd^{2+}$	$6.31 \times 10^{-4}$	3.20	$1.58 \times 10^{-3}$	2.80	$3.55 \times 10^{-3}$	2.45

sources. This appears to have been the case. The results suggest that the peat humic acid (see previous section) formed more stable complexes than the Harpster and Leonardite humic acids, which were the ones used in this particular study. Data obtained earlier for the peat humic acid are included in Table for comparison purposes.

Tentative  $B_3$  values were also obtained for  $\text{Cr}^{3+}$  complexes. These ranged from  $1.5 \times 10^{-4}$  to  $1.0 \times 10^{-5}$ .

(c) Metal Titrations - These experiments involved sequential additions of metal ion to the humic acid at a given pH followed by base titration of the liberated hydrogens (pH returned to initial starting position). Since pH was kept constant, the method permitted estimates to be made for  $K_2$ , using the relationship

$$b_j = K_{ij} k_j$$

where  $K_i$  is the ionization constant at any given pH.

The measurements were carried out at pH 5.0 and at ionic strengths of 0.1, 0.01, and 0.001. Samples included the Sable and Leonardite humic acids. Data obtained previously for the peat and Harpster humic acids were analyzed in a similar manner, thereby permitting comparisons of  $\log K_2$  for all humic acids.



A few experiments were carried out at pH's of 4 and 6 but this work has not been completed.

Plots of ligand sites bound in the complexes ( $\text{MA} + 2\text{MA}_2$ ) to metal ion concentration provided information on the capacity of humic acid to bind metal ions at any given pH and ionic strength. Typical results are shown in Figures 43 and 44.

The retention capacity of any given humic acid for metal ions was influenced by pH and ionic strength, and followed the order:



The first increments of added metal formed soluble complexes. After saturation of reactive sites, additional metal ions were held by an ion-exchange mechanism, in which case precipitation of the humic acid occurred. In natural soil it would appear that humic acid occurred. Newly formed humic substances would be effective in solubilizing solid phase forms of Pb.

Log  $K_2$  values for the humic acids at pH 5.0 and ionic strengths of 0.1, 0.01, and 0.001 are recorded

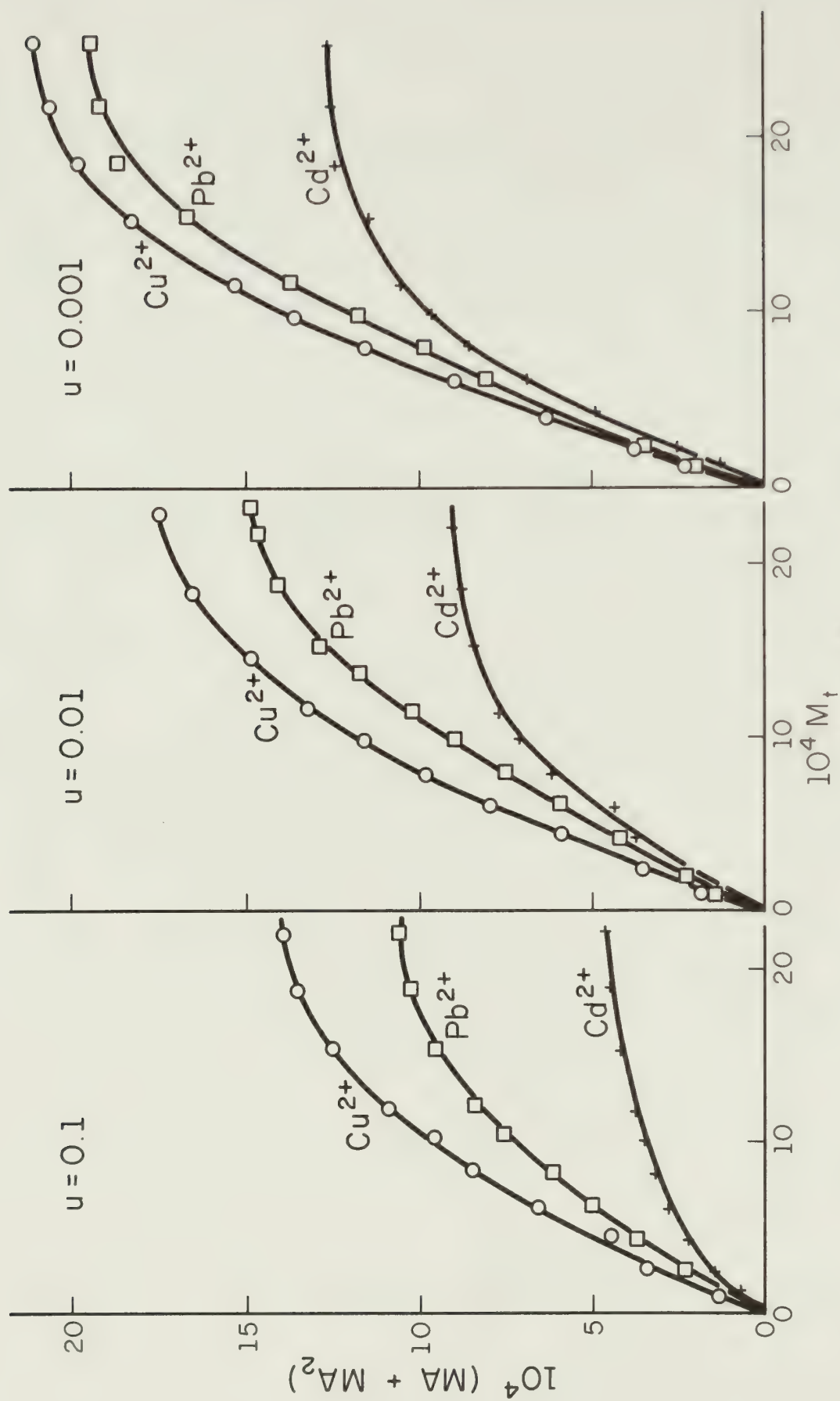


Figure 43

Ligand Sites bound in Metal Complexes vs. Metal Ion Concentration ( $M_t$ ) for Leonardite Humic Acid

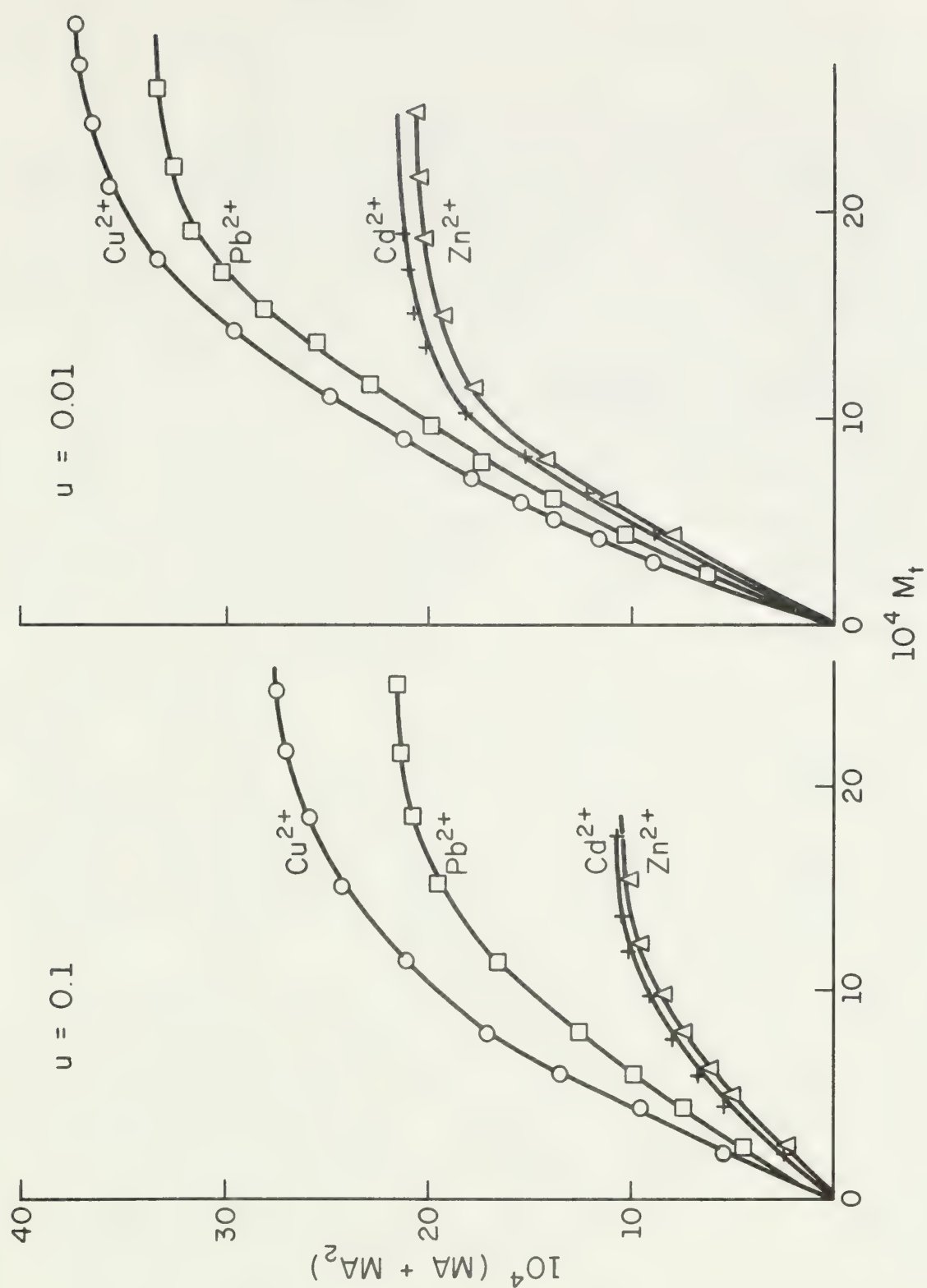


Figure 44

Ligand Sites Bound in Metal Complexes vs. Metal Ion Concentration ( $M_t$ ) for Sable Humic Acid

in Table 29. Data are also included for the peat and Harpster humic acids but it should be emphasized that these data were secured in a different way and cannot be compared directly to the results for the Sable and Leonardite humic acids. In the latter case, more stable complexes were formed with the Sable humic acid. Highly stable  $\text{Pb}^{2+}$  complexes were formed with the peat humic acid. In accordance with the previous studies, stabilities of the complexes increased with decreasing ionic strength and followed the order:



Tentative data were also obtained for  $\text{Cr}^{3+}$  complexes with the Leonardite humic acid.  $\log K_3$  values were 7.6, 8.2, and 9.8 at ionic strengths of 0.1, 0.01, and 0.001, respectively.

Thus, results have been obtained on the stabilities of metal complexes with humic acids which should lead to a better understanding of the role of organic constituents in binding toxic heavy metals. Additional studies are underway.

Table 29

Stability Constants (Log  $K_2$ ) for Complexing of Metal Ions  
by Four Humic Acids at pH 5.0

$M^{+n}$	Ionic Strength ( $\mu$ )		
	<u>0.1</u>	<u>0.01</u>	<u>0.001</u>
Peat Humic Acid			
Pb <sup>2+</sup>	6.9	7.4	-
Sable Humic Acid			
Cu <sup>2+</sup>	6.6	7.1	8.3
Pb <sup>2+</sup>	6.0	6.5	7.8
Cd <sup>2+</sup>	5.4	6.0	7.2
Zn <sup>2+</sup>	5.8	6.0	7.1
Harpster Humic Acid			
Cu <sup>2+</sup>	5.5	6.3	6.9
Pb <sup>2+</sup>	5.4	6.2	6.8
Cd <sup>2+</sup>	5.1	5.8	6.5
Leonardite Humic Acid			
Cu <sup>2+</sup>	6.1	7.0	7.8
Pb <sup>2+</sup>	5.9	6.5	7.4
Cd <sup>2+</sup>	5.3	6.0	6.6

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## 6. Solubility Considerations of the Lead Orthophosphate and Lead Pyrophosphate

Precipitation of lead phosphates from  $\text{Na}_4\text{P}_2\text{O}_7$  and/or  $\text{Na}_3\text{PO}_4$  solutions with lead nitrate was studied at pH 6.5.

Lead pyrophosphate was found to precipitate prior to lead orthophosphate upon addition of lead nitrate to equimolar ( $\sim 9\text{mM}$ ) solutions of  $\text{Na}_4\text{P}_2\text{O}_7$  and  $\text{Na}_3\text{PO}_4$ . Pulse polarographic study of a solution initially  $6.82 \times 10^{-4}\text{M}$   $\text{Pb}(\text{NO}_3)_2$  and  $9.1 \times 10^{-3}\text{M}$   $\text{Na}_4\text{P}_2\text{O}_7$  showed less than  $2 \times 10^{-6}\text{M}$   $\text{Pb}^{++}$  and  $1.45 \times 10^{-5}\text{M}$   $\text{PbP}_2\text{O}_7^{--}$  concentration and the computed equilibrium concentration of  $\text{P}_2\text{O}_7^{4-}$ , the solubility product of lead pyrophosphate was calculated

$$[\text{Pb}^{++}]^2 [\text{P}_2\text{O}_7^{4-}] = 1.5 \times 10^{-27}$$

The low solubility product of lead pyrophosphate above suggests that the lead pyrophosphate precipitation at pH 6.5 can be favored over lead orthophosphate even when the total orthophosphate concentration exceeds that of pyrophosphate. This observation has particular significance in explaining the formation of lead orthophosphate and lead pyrophosphate in plants grown in lead rich media.

## 7. Studies of Heavy Metal Adsorption by Hydrous Oxides

### Background

Hydrous oxides of iron, aluminum and manganese are common occurrences in soils and sediments and they are cited often as the significant controls on the distribution and transport of heavy metals in the environment. Among the various adsorbents for heavy metals found in the sea, Krauskopf, 1956, reported that iron and manganese (hydrous) oxides are most effective. Jenne in 1968 wrote an excellent review on the heavy metals and hydrous oxides in soils and water. The  $E_h$  and pH effects on the "available" heavy metal ions in soils and sediments, Jenne points out, in most cases could be the indirect effect of the changes in iron and manganese species. For example, the reduction of hydrous iron or manganese oxide may solubilize them and the heavy metals adsorbed on hydrous oxides are released. Similar relationship between heavy metals and hydrous oxides exists in all natural waters and its significance was discussed by Morgan and Stumm (1965).

The scavenging nature of hydrous oxide towards heavy metals is well known. Extremely high concentrations of Co and Ni found in manganese nodules in ocean bottoms is an end result of long time scavenging from sea water. In analytical chemistry scavenging by hydrous oxides has been used

for collecting radionuclides, transuranium elements, and heavy metals present in small amounts in large volume solutions. In spite of the role of the sorption on hydrous oxides in so many laboratory and natural systems very little work was carried out in evaluating the factors that affect the sorption process. Kolthoff and his co-workers and also Kurbatov and his co-workers studied the adsorption (and coprecipitation) of some divalent metal ions by hydrous ferric oxide (HFO) in ammoniacal medium. At constant solution volume, the adsorption was reported to increase with the amounts of HFO, metal ion being studied and  $\text{NH}_3(\text{pH})$ . Divalent metal ions that form ammine complexes showed decreased adsorption with increase in ammonium chloride concentration. Within a short pH range (about 2 pH units), the adsorption was found to change dramatically and the exact pH range over which the change takes place depended on the metal ion studied. Dramatic change in adsorption with pH was also reported during adsorption of divalent ions on hydrous manganese and iron oxides (Kurbatov et al. 1951, Kozawa 1961). Hydrogen ion was released in most cases during the adsorption and the ratio hydrogen ions released/metal ion adsorbed was rarely integral. In the pH range 4 to 9, Lockwood and Chen (1973) found that the mercury uptake by

hydrous manganese oxide does not release  $H^+$  into solution. This abnormal behavior of mercury was explained by considering  $Hg(OH)_2$  rather than  $Hg^{++}$  as the adsorbing species.

In Pr-3 and also in a recent communication (Gadde and Laitinen, 1973a), we presented the results of lead adsorption studies on HFO. In the pH range commonly found in nature, 4 to 8, lead adsorption was found to vary significantly and as much as 0.28 moles lead per mole HFO (HFO expressed in terms of Fe) was found to be adsorbed at pH 6. Also specific adsorption rather than counter-ion type adsorption was involved in lead adsorption on HFO. Because of the extreme environmental importance we extended the lead adsorption studies on HFO to other hydrous oxides and other cations. The hydrous oxides of iron and manganese were used in most of the work due to their ease in preparation and stability at least over periods of several days. Hydrous aluminum oxide was found to vary in its adsorption behavior with time so only a limited study was made using it. The cations  $Cd^{++}$  and  $Tl^+$  besides lead were selected for study due to their known toxicity to human beings and  $Zn^{++}$  was selected for its importance in agriculture. (Zinc is a required nutrient for plants but known to be toxic at higher concentrations).

## 2. Experimental

Hydrous manganese oxide (HMO) was prepared by slowly adding manganese (II) nitrate solution to alkaline permanganate solution. The amounts of manganese (II) nitrate, potassium permanganate, and sodium hydroxide mixed were in the mole ratio 3:2:4. By using these ratios, Morgan and Stumm (1964) found the product to have the composition  $\text{MnO}_x$  where  $x$  varied from 1.90 to 1.95. Before using this HMO in adsorption studies, it was filtered, washed with and re-dispersed in distilled water, adjusted to pH 6, made up to the desired volume, and aged for 16 to 20 hours. X-ray studies showed that the HMO prepared is of amorphous nature. A known aliquot of the HMO suspension was used in the individual experiments. Amount of HMO expressed in the data reported below is taken as the same as the moles Mn present in the aliquot. The latter quantity was calculated from the total manganese used in making HMO.

Hydrous oxides of iron and aluminum were prepared by titrating the nitrate solutions to pH 6 with NaOH (PR-3). Hydrous ferric oxide (HFO) was then washed and aged as described under HMO. Hydrous aluminum oxide (HAO) was not easily filtered or centrifuged, so the washing step was eliminated. The amount of  $\text{NaNO}_3$  left in HAO amounted to approximately 0.02 M in the final solution used for sorption



study. As in the case of HMO, the amounts of HFO and HAO were calculated from the initial amounts of Fe and Al used in making these hydrous oxides.

In obtaining the adsorption data, known amounts of hydrous oxide and the metal ion of interest were equilibrated for three hours at a predetermined pH. Metal ion concentration in solution at the end of the equilibration period was determined by pulse polarography. The amount of metal ion adsorbed was then computed from the amount initially added and the amount left at equilibrium. Further details of the procedure can be found elsewhere (PR-3). Sorption equilibrium with HFO was found to be nearly complete in about 10 minutes but in the case of HMO more than 30 minutes was needed.

Princeton Applied Research Corporation, Model 174 Polarographic Analyzer was used to do the pulse polarographic determinations.

### 3. Results

#### Effect of pH

The adsorption of lead, zinc, cadmium, and thallium (I) ions on hydrous oxides of manganese and iron was studied and the results are shown by the plots in Figures 45 and 46.

On hydrous manganese oxide the adsorption of lead, cadmium, and zinc was favored with increases in pH. The extent



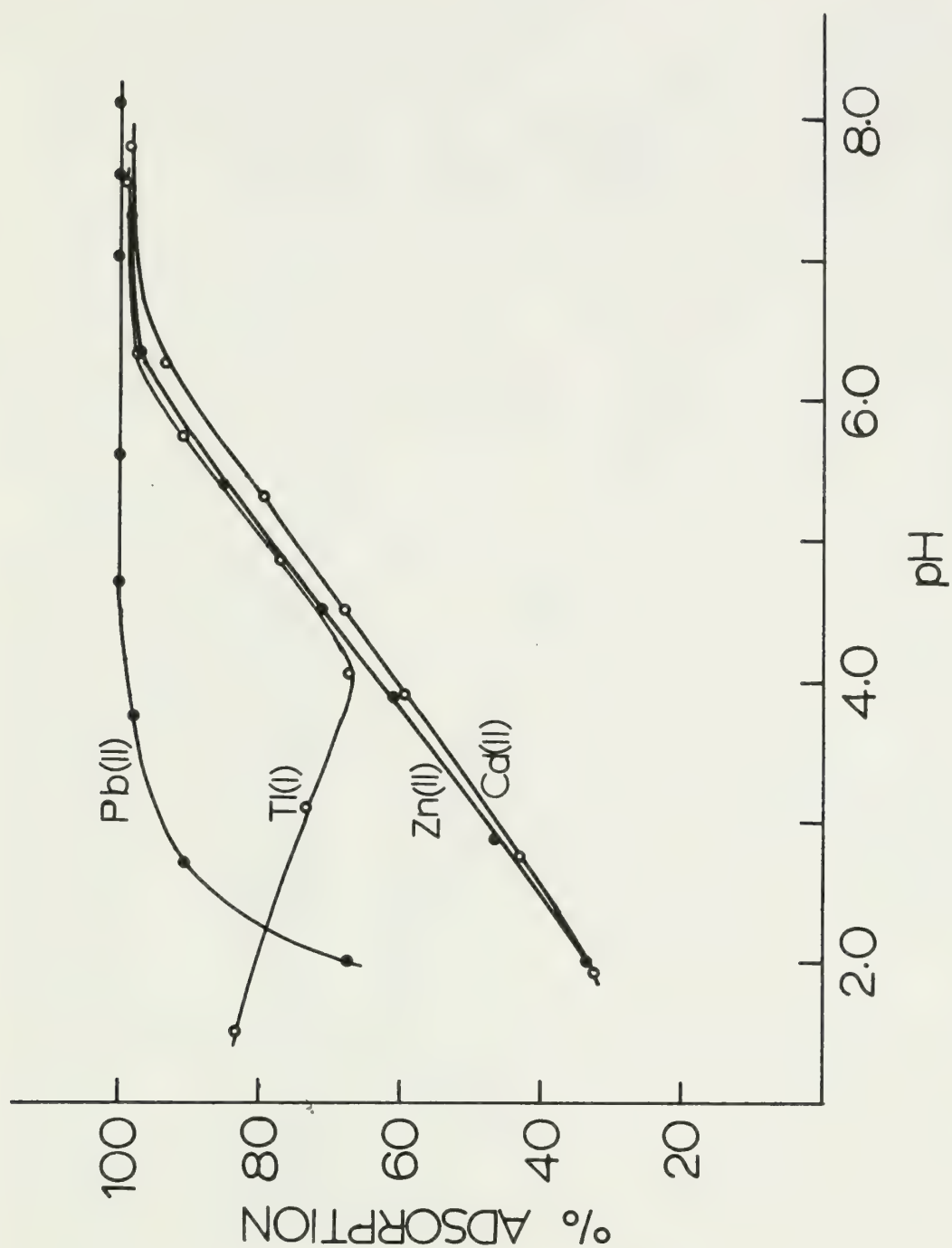


Fig. 45 Effect of pH on the Adsorption of Heavy Metal Ions on Hydrous Manganese Oxide (HMO)  
HMO: 0.436 mmole. Heavy metal ion: 0.1 mmole.  
Solution Volume: 100 ml.

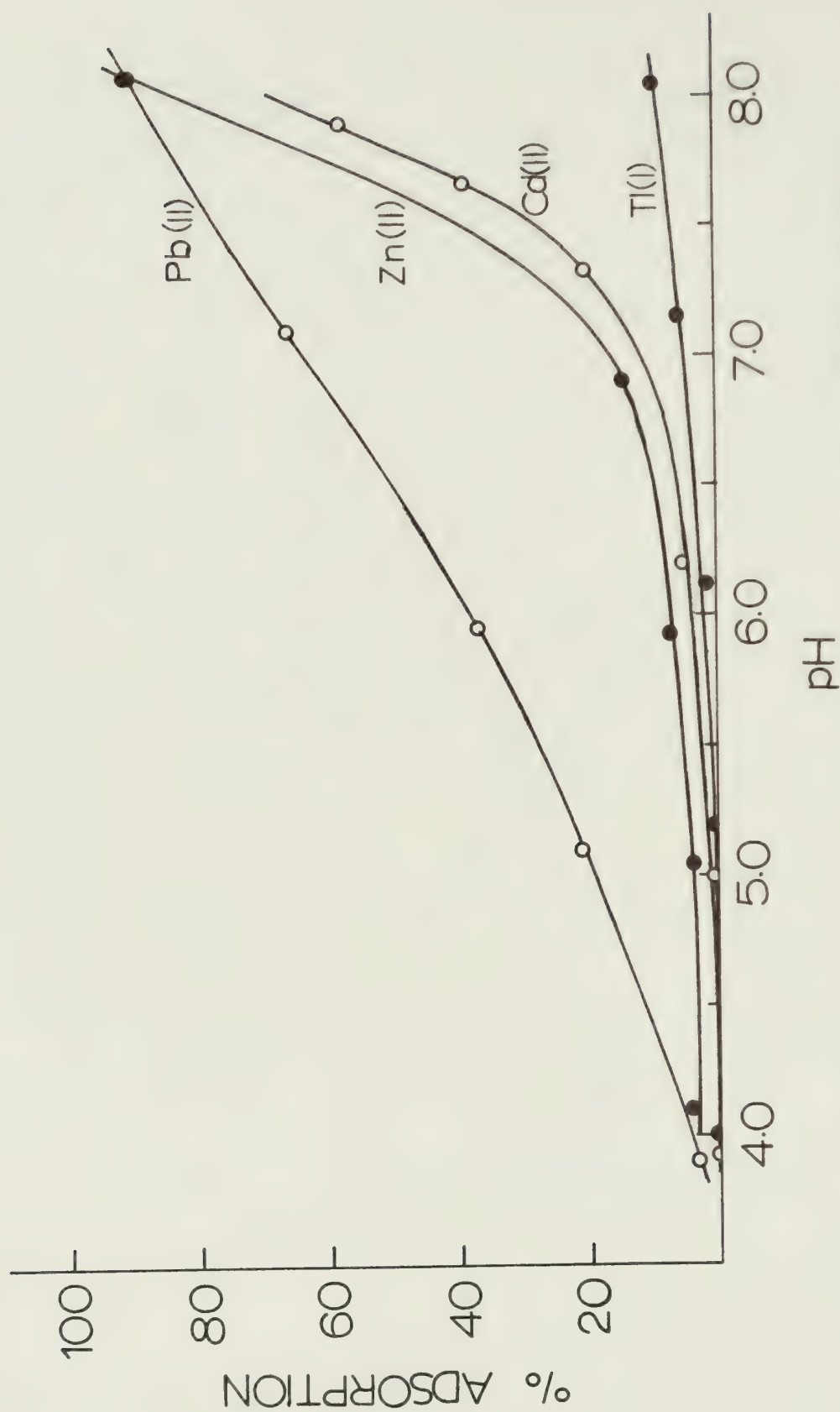


Fig. 46 Effect of pH on the Adsorption of Heavy Metal Ions on Hydrous Ferric Oxide (HFO)  
 HFO: 0.625 mmole. Heavy Metal Ion: 0.1 mmole.  
 Solution Volume 100 ml.

of adsorption was found to follow the order  $Pb > Zn > Cd$  at any given pH in the pH range 2 to 8. Lead showed considerable adsorption even at pH 2 and virtually 100% adsorption was achieved at  $pH > 4.5$ . The percent adsorption of zinc and cadmium showed a rather linear increase with pH in the adsorption region 30 to 90%. At  $pH > 4$  thallium adsorption vs. pH plot was similar to that of zinc and cadmium but a reverse in adsorption trend was observed at  $pH < 4$ . The apparent increase in thallium adsorption at  $pH < 4$  appears to be due to a redox reaction between  $Tl(I)$  and hydrous manganese oxide forming  $Tl(III)$  and a soluble manganese species which is colorless. At pH 2, the reaction of 4 mM  $Tl(I)$  and hydrous manganese oxide was found to bring considerable amount of manganese into solution that can easily be detected by oxidation to permanganate. Solubilization of hydrous manganese oxide was also enhanced by lead and cadmium but to a much lesser extent.

Favored adsorption of lead, cadmium, and zinc at higher pH values was also observed on hydrous ferric oxide (Figure 46). At  $pH < 8$ , thallium adsorption was found to be small ( $< 10\%$ ) while the adsorptions of lead, cadmium, and zinc were substantial, especially at pH 7 and above.

Figure 47 shows the adsorption vs. pH plots for lead on hydrous oxides of manganese, iron, and aluminum obtained

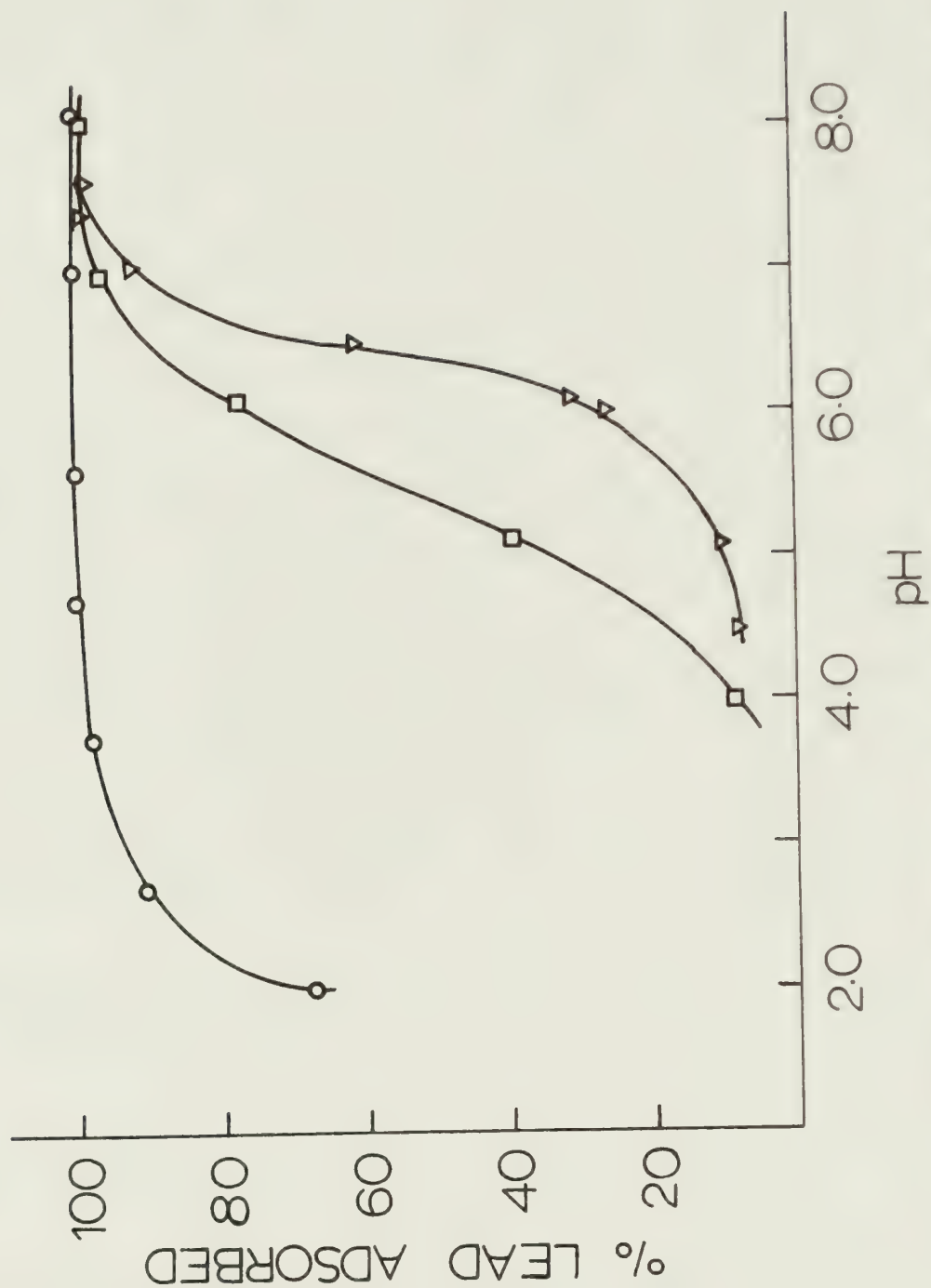


Fig. 47 Effect of pH on the Adsorption of Lead on Hydrous Oxides  
 Lead: 0.1 mmole. Solution Volume: 100 ml.  
 ○ Hydrous Manganese Oxide, 0.436 mmole.  
 □ Hydrous Ferric Oxide, 0.639 mmole.  
 ▼ Hydrous Aluminum Oxide, 0.629 mmole.

under similar conditons. The plots clearly show that hydrous manganese oxide is most effective in removing lead from solution and the hydrous ferric oxide and hydrous aluminum oxide follow. Under the experimental conditions used in Figure 47, the lead adsorption at pH 6 amounted to 100, 47, and 27% for the hydrous oxides of manganese, iron, and aluminum respectively.

The pH dependent adsorption of cadmium and zinc on hydrous manganese oxide is, to a large extent, a reversible process. The adsorption equilibrium of cadmium-hydrous manganese oxide at pH 2 was reproduced within experimental error when the pH was shifted to pH 7.8 and brought back to pH 2 again after three hours. Similar observation was made with zinc--hydrous manganese oxide also, in which the pH shift was made from 2 to 5.4 and back to 2. The data on the reversibility of lead adsorption with pH on hydrous ferric oxide was already reported (PR-3).

Because of the Langmuir or Freundlich type adsorption of metal ions on hydrous oxides reported below, the percent adsorption vs. pH plots are very much dependent on the relative amounts of hydrous oxide and the metal ion (e.g. see PR-3, Fig. 24). So a comparison of these plots should be made only when the data are obtained under identical conditions.

### Effect of Metal Ion Concentration

The variation in the adsorption of zinc, cadmium, lead, and thallium on hydrous manganese oxide with their equilibrium concentration in solution is shown in Figure 48. At concentrations 1 mM and above, cadmium, zinc, and thallium adsorption reached a limiting plateau region indicating that the adsorption capacity of hydrous manganese oxide for the particular ion has been reached. At pH 6, the adsorption capacities determined from the data in Figure 48 are 0.17, 0.24, and 0.28 moles/mole hydrous manganese oxide for the metal ions: cadmium, zinc, and thallium respectively. In the case of lead, limiting plateau in adsorption was not observed up to a lead concentration of 1.5 mM in solution and the adsorption capacity value apparently is larger than the maximum adsorption observed, 0.56 moles/mole hydrous manganese oxide.

### Competitive Adsorption of Metal Ions

Table 30 summarizes the data obtained in experiments in which two metal ions were adsorbed at pH 6 on the same hydrous manganese oxide sample. The metal ion that is adsorbed first on hydrous manganese oxide is listed first in the first column in Table 30. For comparison, the percent adsorption of cadmium, zinc, and thallium found independently without the competition from lead are also listed in the last



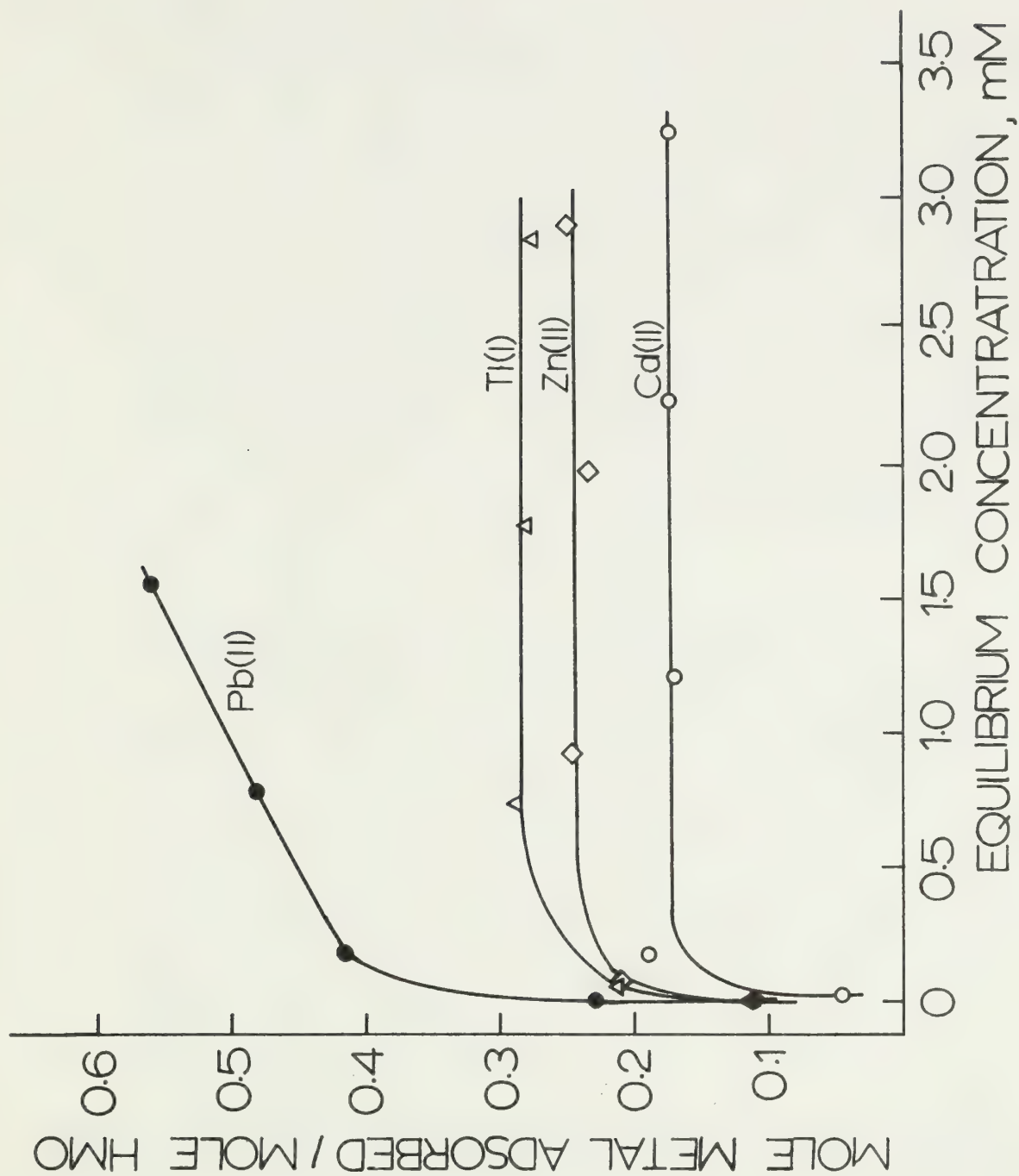


Fig. 48 Effect of the Heavy Metal Ion Concentration at Equilibrium on its Adsorption on Hydrous Manganese Oxide  
HMO: 0.436 mmole

Table 30

Competitive Adsorption of Metal Ions on Hydrous Manganese  
Oxide

Hydrous Manganese Oxide 0.436 mmoles

Lead and Other Ions 0.1 mmole (each)

Solution Volume 100 ml

<u>Competing Ions</u>	<u>Percent Adsorption</u>		<u>Percent Adsorption in the Absence of Lead</u>
	<u>Lead</u>	<u>Other Ion</u>	
Pb, Cd	99.9	18.2	82.3
Cd, Pb	99.9	16.8	
Pb, Zn	99.9	22.8	91.9
Zn, Pb	99.9	22.4	
Pb, Tl	100	35.5	93.4
Tl, Pb	100	35.5	
Pb, Ca	100	-	-
Pb, Ca <sup>1</sup>	100	-	-
Pb, Mg	100	-	-
Pb, K <sup>1</sup>	100	-	-

<sup>1</sup>Ca and K in these cases were 1 mmole each.

column of Table 30.

The data in Table 30 clearly indicate that at pH 6, lead is adsorbed much more strongly than all the other metal ions studied. Except in the case of cadmium there is little variation in adsorptions of the competing ions whether lead adsorption occurred first or after the sorption of the other ion. It follows then that the adsorption processes are reversible and they can be replaced by other competing metal ions. At equilibrium, the concentration of lead in solution was less than 2  $\mu\text{M}$  and those of other ions are more than 600  $\mu\text{M}$ .

#### Hydrogen Ion Release During Adsorption

Simultaneous with the adsorption of metal ions on hydrous oxides, a decrease in the pH of the solution was observed. In order to quantify the relation between the adsorption of metal ions and the  $\text{H}^+$  released, the pH of the solution was readjusted to the initial pH with standard NaOH (PR-3). On hydrous manganese oxide the ratios, the number of  $\text{H}^+$  released per metal ion adsorbed, were found to be 1.4, 1.3, 1.1, and 0.38 for the metal ions, lead, cadmium, zinc, and thallium respectively. These ratios were obtained at pH 6 and they may be different if the adsorptions were to be carried at other pH values. For lead adsorption on hydrous ferric oxide, the ratios found were 1.2 and 1.6 at

pH's 5 and 6 respectively (PR-3). In all cases studied, the ratios were nonintegral.

#### Effect of Aging

The effects of aging hydrous oxides before the adsorption of lead and also the effect of aging hydrous oxide in the presence of lead were studied. The results obtained with hydrous ferric oxide are presented in Table 31. Lead adsorption appears to decrease with aging of the hydrous ferric oxide but as the data in Table 31 show, the trend is not very smooth or continuous. Aging  $Pb^{++}$ -hydrous ferric oxide mixture may have some enhancing effect on lead adsorption but again, the data here also greatly fluctuate.

The percent recovery values given in the last column of Table     were obtained by separating the lead adsorbed hydrous ferric oxide, redispersing it in 100ml water and adjusting the solution pH to 2. The amount (%) of total lead originally held by hydrous ferric oxide that is brought back into solution was reported. Here also, both types of aging though appear to decrease the recoverability (reversibility with pH) of lead, the trend is not very conclusive.

#### Lead Uptake by Hydrous Ferric Oxide-Clay Mixtures

Lead uptake by hydrous ferric oxide-clay mixtures compared to the sum total of lead uptake by the components of the mixture was studied. Montmorillonite, kaolinite, and

Table 31

Aging Effect on Lead Sorption on Hydrous Ferric Oxide

Hydrous Ferric Oxide      0.625 mmole

Lead                              01. mmole

Solution Volume              100 ml

pH                                6

Aging Time Hours		<u>Percent Lead Sorbed</u>	<u>Percent Lead Recovered</u>
<u>HFO</u>	<u>HFO+Pb</u>		
20	3	88.7	81
44	3	87.8	72
92	3	80.1	73
164	3	80.9	-
352	3	82.0	69
660	3	74.9	68
20	27	80.3	64
20	75	91.9	69
20	147	95.9	68
20	335	94.4	59
20	643	92.0	56

illite were selected for these studies as representative clay types. Using hydrous ferric oxide (HFO) preaged for 24 hours at pH 6, the HFO-montmorillonite mixture was found to take up 25% more lead over the predicted amount. In similar studies, lead uptake by HFO-kaolinite mixture was found to be 27% less than the predicted value while the HFO-illite mixture took up lead as predicted.

In separate experiments, HFO was precipitated in the presence of clay material and the mixture aged for 24 hours prior to lead uptake study. Mixtures of HFO with kaolinite or illite in these studies took up lead as predicted. HFO-montmorillonite mixture showed an increase in lead uptake by about 25%.

Enhancement of lead uptake found with HFO-montmorillonite mixture is probably due to an increased surface area of HFO by adsorption on montmorillonite. The lead uptake behavior by HFO-kaolinite mixtures is quite peculiar and it appears to be governed by phenomena with opposing lead uptake trends.

#### 4. Discussion

Hydrous oxides in aqueous solutions carry a surface charge which is very pH dependent. The pH of zero point of surface charge (PZC) and the pH of the solution relative to PZC affects the counter-ion type adsorption of cations or



anions. At pH values higher than PZC, cation adsorption is generally favored. Similarly anion adsorption is favored by pH values less than PZC.

Morgan and Stumm (1964) reported a PZC of  $2.8 \pm 0.3$  for the type of hydrous manganese oxide used in our work. For  $\delta$  -  $\text{MnO}_2$  and manganous manganite (probable components of hydrous manganese oxide), PZC values were reported by others (Murray et al. 1968) to be  $1.5 \pm 0.5$  and  $1.8 \pm 0.5$  respectively. The adsorption data of lead, cadmium, and zinc at pH 2 (Figure 45) and any reasonable extrapolation of the data to lower pH values indicate that there is finite adsorption in the vicinity of PZC (1.5 to 2.8). This behavior can only be attributed to the specific adsorption of these metal ions on hydrous manganese oxide. The behavior of thallium adsorption at  $\text{pH} > 4$  similar to that of cadmium and zinc is also probably due to the specific adsorption than simple counter-ion type adsorption. Specific adsorption of  $\text{Ni}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{Co}^{++}$  on manganous manganite was reported earlier by Murray, et al.

The apparent increase in thallium adsorption on hydrous manganese oxide at  $\text{pH} < 4$  is interesting. Such a trend in adsorption on hydrous oxide was not reported before. Murray et al. reported the adsorption of cobalt on manganese(II) manganite and the amount adsorbed vs. pH plot

showed a decrease in slope at  $\text{pH} < 2$  while the plots for copper and nickel showed an increase in slope. In the case of thallium (probably in the case of cobalt also) there appears to be a redox reaction between hydrous manganese oxide and thallium to form  $\text{Tl(III)}$  and  $\text{Mn(II)}$  species. Thallium(III) could either be adsorbed strongly on hydrous manganese oxide or form thallium(III) hydroxide which has very low solubility ( $K_{\text{sp}} = 1.5 \times 10^{-44}$ ).

Calculations using the standard potential data for  $\text{MnO}_2/\text{Mn(II)}$  and  $\text{Tl(III)}/\text{Tl(I)}$  showed that the redox reaction between  $\text{MnO}_2$  and  $\text{Tl(I)}$  is highly favorable thermodynamically.

The PZC values for different oxides and hydroxides were tabulated by Parks. The PZC values listed for hydrous ferric oxide and hydrous aluminum oxide prepared by methods similar to those described above are 8.5 and 7.5 respectively. At PZC, lead adsorption was finite (Figure 47) on both these hydrous oxides suggesting that specific adsorption is involved. The plots in Figure 46 indicate that specific adsorption is involved in the adsorption of zinc and cadmium also on hydrous ferric oxide. At about pH 7, the hydrolysis of  $\text{Zn(II)}$  becomes significant and the apparent adsorption reported in Figures 45 and 46 at these

pH values are partly due to the loss of Zn(II) as its hydroxide.

Both Freundlich and Langmuir type adsorptions were found to explain the adsorption of certain metal ions on hydrous oxides. Kolthoff et al. reported that copper, nickel, and zinc adsorptions on hydrous ferric oxide in ammoniacal medium follows the Freundlich isotherm. The adsorption of Mn(II) on hydrous manganese oxide was reported to follow the Langmuir isotherm (Morgan and Stumm 1964). Our data did not follow either one of these isotherms. (Figure 48). Also with the increase in concentration of divalent ions (data plotted in Figure 48) increase in flocculation was noticed roughly at and above 0.5 mM.

The release of hydrogen ions during the adsorption of metal ions on hydrous oxides was reported earlier by many workers. The actual mechanism of the change in surface charge of hydrous oxide with pH and also that of the adsorption of metal ion on hydrous oxides is still not clear. The adsorptions can be treated either as surface complex formation or as ion exchange process (Morgan and Stumm). The nonintegral ratio of  $H^+$  released per metal ion adsorbed observed suggests that the exchange or replacement of  $H^+$  by metal ion does not have 1:1 type relation. In the case of lead it was shown (PR-3) that very little hydrolysis of

$\text{Pb}^{++}$  occurs at pH 6 and that the adsorption mainly involves  $\text{Pb}^{++}$  only. Similarly it can be shown that the hydrolysis of  $\text{Cd}^{++}$ ,  $\text{Zn}^{++}$ , and  $\text{Tl}^+$ , though play a prominent role at about pH 7 or above, the adsorptions at low pH values mainly involve the unhydrolyzed species. The nonintegral ratios are not peculiar to hydrous oxides and metal ions reported above, earlier workers (Morgan and Stumm 1964, Kozawa 1961) found similar values, some as high as 4, with other hydrous oxides (and oxides) and other metal ions.

The reversible nature of the adsorption of metal ions on hydrous oxides is of great environmental significance. The metal ions adsorbed on hydrous oxides, as shown above, are very sensitive to pH. Higher pH values generally favored the adsorption and desorption was favored at low pH values. Among the three hydrous oxides studied and commonly found in nature, hydrous manganese oxide is very effective in adsorbing metal ions and holding them for over a wide pH range. In the pH range of most natural environments, 4 to 8, the adsorptions on hydrous ferric and aluminum oxides are quite sensitive to pH. Depending on the fluctuations in pH, hydrous ferric and aluminum oxide act as scavengers or source of metal ions and affect the metal ion concentrations in solution phase rather dramatically with pH. In the regions of acid-mine run offs and red mud from

alumina plant wastes, hydrous oxides are present in large amounts and heavy metal ion control by hydrous oxide become extremely important. Even at pH values favorable for toxic metal ion adsorptions on hydrous oxides, the dangers of toxicity to aquatic organisms and fishes are not eliminated. Hydrous oxides with sorbed toxic metal ions in high concentrations may be taken directly from fine sediment particles, floating or settled to the bottom in the aquatic environments. Plant roots are known to exude some organic compounds that have metal complexing properties (Gadde and Laitinen 1973b). Metal ions adsorbed on hydrous oxides can serve as an excellent source of their nutrient elements like zinc but at the same time can provide toxic metals as well.



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- C. Lead and Cadmium Uptake by Corn and Soybeans from  
Soils with Varying Characteristics  
(PRD 103 - 104, 110)

Background

A previous study on lead uptake and toxicity demonstrated that corn plants will accumulate large amounts of lead when supplied to them in sand culture (Miller and Koeppel, 1971). The same study demonstrated that as little as  $24\mu\text{g Pb/g}$  of sand caused a stunting of growth under phosphate deficient conditions. Several workers have indicated that although the lead content of soil is raised substantially, the lead accumulation of plant tops remains quite low (e.g. Kloeke and Riebartsh, 1964; MacLean et al., 1969; Marten and Hammond, 1966; Baumhardt and Welch, 1972). However, other workers have found substantial accumulation due to soil contamination (Jones and Hatch, 1945; Rolfe, 1973; Warren and Delavault, 1962). John (1972) attempted to correlate lead uptake of lettuce and oats to soil properties and found that soil pH was an important parameter in predicting plant lead, although no relationship with organic matter was observed. Rolfe (1973) demonstrated that soil phosphate levels affected lead uptake by tree seedlings and suggested that further research should be done on soil factors affecting lead mobility.

Research by J. J. Hassett on this project has shown that the lead and cadmium sorption capacity of soil varies widely for different soil types. Although these data have some predictive value relating to plant availability, actual plant accumulation from these soils should be determined.

Cadmium uptake and toxicity to plants is well documented (John, Van Learhoven, and Chuah, 1972; Haghiri, 1973; Turner, 1973; Jones, Hinesly, and Ziegler, 1973; Page, Bingham, and Nelson, 1972; Root, Koeppe, and Miller (manuscript)). It appears from these studies that Cd is more toxic than Pb and probably more mobile in the soil and plant. However, as with Pb the soil conditions affecting its uptake by plants need to be further described.

The following report describes a study presently underway to define the importance of several soil parameters on the uptake and plant toxicity of soil contaminated with lead and cadmium. In addition, results of preliminary experiments concerning the effects of lead on seed germination are included.

#### Experimental

Native Illinois agricultural soils were selected which exhibit a range in three characteristics believed to be important in the plant uptake of cations. The three soil

parameters are cation exchange capacity (CEC), pH, and available phosphorus (Bray  $P_1$  value). Table 32 lists the range of values in these 3 parameters that the experimental design was based on. Table 33 gives the 3 values for each of the soils. The total sorptive capacity of the soil (CEC) is expressed as meq/100 g of soil and includes the contribution of both clay colloids and organic materials. The range in the soils selected is from 2.3 to 30.3 meq/100 g of soil. In the CEC series the soil pH and  $P_1$  levels were within the optimum range for growth of corn and soybean. The pH series had soils ranging from pH 4.5 to pH 7.9. In this series the CEC was uniform at between 6 to 8 meq/100 g soil and  $P$  values were within the optimal range for plant growth. For determination of  $P_1$  effects the range was 9 to 107 lbs P/acre-6" of soil with CEC values of 6 to 8 and soil pH's within the optimal range. Soil #5 appears in each of the three series and thus there are a total of 10 different soil conditions. Each of the 10 soils was treated with  $PbCl_2$  at 250, 500, 1000 or 2000 mg Pb/kg of soil or  $CdCl_2$  at 1, 10, and 100 mg Cd/kg of soil. A control with no added metal was included.

An additional parameter, the effect of residence time of the metal in the soil, was included in the design. All

Table 32

Soil variables in Pb and Cd uptake studies. Ten soils were obtained with a range in CEC, soil pH and  $P_1$  values. For the CEC series the soil pH, and Bray  $P_1$  values were within the optimum range for growth. Similarly, for the soil pH and Bray  $P_1$  series the other values were within the optimum range.

Cation Exchange Capacity (CEC) (meq/100 g soil)	Soil pH	Bray $P_1$ Test <sup>1</sup> (lbs/acre-6")
2.3 (#10) <sup>3</sup>	4.5 (#1)	9 (#6)
7.9 (#5)	6.0 (#5)	32 (#11)
15.9 (#8)	7.0 (#4)	64 (#5)
30.3 (#9)	7.9 <sup>2</sup> (#4L)	107 (#3)

<sup>1</sup>Measure of available phosphorus.

<sup>2</sup> $\text{CaCO}_3$  (1%) added to bring pH up.

<sup>3</sup>Values in parantheses refer to the code number of the soils.

Table 33  
 Characteristics of Experimental Soils

Soil #	Soil Series	Description	CEC	Bray P <sub>1</sub>	pH
1	Cisne	Silt Loam	6.8	82	4.5
3	Cisne	Silt Loam	8.5	107	6.1
4	Cisne	Silt Loam	6.7	33	7.0
4L	Cisne	Silt Loam	6.7	33	7.9*
5	Cisne	Silt Loam	7.9	64	6.0
6	Cisne	Silt Loam	7.7	9	5.5
8	Sidell	Silt Loam	15.9	76	6.5
9	Drummer	Silty Clay Loam	30.3	44	6.1
10	Bloomfield	Loamy Sand	2.3	125	5.7
11	Cisne	Silt Loam	6.7	32	6.4

\*Soil 4 with 1% CaCO<sub>3</sub> added



of the soils were prepared at the same time by addition of the metals as powders and thoroughly mixing the soils. The soils were placed in 4" plastic pots (three duplicate pots were prepared) and maintained at field capacity for two weeks so that the metal would be sorbed by the soil colloids. Even the highest metal concentrations did not exceed the sorption capacity of the soils. The pots were separated into 4 groups that will be planted to corn (Wf9xM14) and soybean (Amsoy) at intervals of time (2 plants per pot). The planting schedule is 2 weeks, 3 months, 6 months, and 9-12 months after the initial wetting of the soil. The plants not planted at the initial 2-week time period will be watered to field capacity every 2 weeks, and allowed to dry to simulate field conditions.

Thus, the total number of pots involved is. 10 soil variables x 8 metal concentrations x 2 plant species x 3 duplicate pots x 4 aging periods = 1920 pots. The plants are grown for a period of 4 weeks for corn and 6 weeks for soybean, and then harvested. Plant parts are separated into roots and shoots for separate analysis. The roots are washed in distilled water and 0.1 N EDTA to remove surface metals. The analyses made on the plant material are fresh weight, dry weight, metal content, phosphate content for the

Pb treatments, and Zn and Fe content for the Cd treatments. The soils are saved for determinations of extractable Pb and Cd and other soil analysis for correlation with plant uptake (See J. Hassett).

## RESULTS

### Effects of Pb and Cd on Growth of Corn Shoots

As of the date of this report, only preliminary results are available. Tables 34 and 35 summarize the fresh and dry weights of the corn shoots from the first Pb and Cd runs.

A trend toward reduction of fresh and dry weights at increasing soil Pb concentrations is evident in several of the soils. The most dramatic decreases in plant growth were in the loamy sand (#10) and the acid silt loam (#1), as would be predicted due to the low CEC in soil #10, and the more ready movement of Pb in acid soils. The fresh weights decreased with increasing Pb in all of the Cisne silt loam soils except soil #5. The dry weights did not strictly follow the trend of the fresh weights in Cisne soils. #4L, #5, and #6. In soils #8 and #9 there were no significant effects of Pb on fresh or dry weights. These two soils had the highest capacity to sorb lead.

### Result A

At very low PI levels the uptake of lead by corn was the greatest (Figure 49). Low soil pH similarly resulted in the greatest uptake (Figure 50). Of the soil variables so far considered the sorptive capacity of the soils (CEC) pro-

Table 34

Fresh and dry weights of 4 week-old corn shoots grown in Pb amended soils. The weights are of 2 shoots grown in the same pot. Each value is the mean of three duplicate pots.

<u>Soil</u>	<u>Pb (ppm)</u>	<u>Fresh Wt. (g)</u>	<u>Dry Wt. (g)</u>
No. 1	250	12.88+0.22	1.33+0.08
	500	12.45+1.48	1.29+0.10
	1000	10.10+3.36	1.12+0.29
	2000	4.32+0.91	0.45+0.11
No. 3	250	20.50+1.09	2.94+0.53
	500	18.94+0.34	2.66+0.56
	1000	18.05+1.60	2.22+0.32
	2000	16.29+0.83	2.13+0.23
No. 4	250	11.73+1.29	1.29+0.22
	500	11.31+0.61	1.29+0.01
	1000	10.60+1.09	1.25+0.12
	2000	8.91+0.54	1.15+0.12
No. 4L	250	9.99+0.40	1.34+0.31
	500	8.74+0.37	0.95+0.08
	1000	8.49+0.81	0.82+0.11
	2000	8.43+0.13	1.06+0.19
No. 5	250	17.42+0.71	1.81+0.02
	500	19.31+0.21	2.00+0.12
	1000	18.60+1.32	1.98+0.25
	2000	16.80+0.91	2.00+0.12
No. 6	250	10.05+0.28	1.12+0.33
	500	8.50+0.79	1.02+0.11
	1000	8.13+0.22	0.92+0.11
	2000	7.46+0.47	1.08+0.07
No. 8	250	12.30+0.76	1.28+0.10
	500	12.23+1.28	1.44+0.13
	1000	11.58+0.83	1.31+0.02
	2000	11.28+1.46	1.16+0.20

Continued Table 34

<u>Soil</u>	<u>Pb (ppm)</u>	<u>Fresh Wt. (g)</u>	<u>Dry Wt. (g)</u>
No. 9	250	17.70+1.73	1.89+0.12
	500	18.44+1.61	1.89+0.17
	1000	18.93+1.09	2.11+0.17
	2000	16.87+2.51	2.00+0.39
No. 10	250	6.65+1.11	0.84+0.17
	500	2.16+0.67	0.35+0.16
	1000	1.16+0.25	0.17+0.08
	2000	0.20+0.11	0.06+0.04
No. 11	250	11.31+0.38	1.20+0.08
	500	10.96+0.67	1.20+0.17
	1000	10.61+0.68	1.21+0.05
	2000	9.92+0.18	1.13+0.04

Table 35

Fresh and dry weights of 4 week old corn shoots grown in cadmium amended soils. The weights are of 2 shoots grown in the same pot. Each value is the mean of 3 duplicate pots.

<u>Soil</u>	<u>Cd(ppm)</u>	<u>Fresh Weight (g)</u>	<u>Dry Weight (g)</u>
#1	0	9.47 $\pm$ 1.16	0.99 $\pm$ 0.07
	1	8.37 $\pm$ 1.45	0.97 $\pm$ 0.07
	10	6.62 $\pm$ 0.54	0.94 $\pm$ 0.13
	100	2.26 $\pm$ 0.58	0.16 $\pm$ 0.02
#3	0	9.83 $\pm$ 0.74	1.12 $\pm$ 0.06
	1	9.76 $\pm$ 0.42	1.34 $\pm$ 0.09
	10	7.23 $\pm$ 0.48	1.16 $\pm$ 0.07
	100	3.28 $\pm$ 0.25	0.53 $\pm$ 0.05
#4	0	5.79 $\pm$ 0.74	0.74 $\pm$ 0.07
	1	5.71 $\pm$ 0.08	0.75 $\pm$ 0.03
	10	4.56 $\pm$ 0.56	0.65 $\pm$ 0.06
	100	1.92 $\pm$ 0.25	0.33 $\pm$ 0.25
#4L	0	5.66 $\pm$ 0.37	0.73 $\pm$ 0.05
	1	6.06 $\pm$ 0.46	0.76 $\pm$ 0.03
	10	5.11 $\pm$ 0.27	0.68 $\pm$ 0.06
	100	2.30 $\pm$ 0.14	0.37 $\pm$ 0.01
#5	0	10.41 $\pm$ 0.60	1.25 $\pm$ 0.05
	1	8.02 $\pm$ 0.42	1.18 $\pm$ 0.28
	10	5.43 $\pm$ 0.64	0.83 $\pm$ 0.06
	100	3.21 $\pm$ 1.05	0.50 $\pm$ 0.15
#6	0	5.90 $\pm$ 0.14	0.75 $\pm$ 0.01
	1	5.66 $\pm$ 0.95	0.77 $\pm$ 0.07
	10	4.29 $\pm$ 0.54	0.64 $\pm$ 0.08
	100	2.38 $\pm$ 0.27	0.38 $\pm$ 0.05
#8	0	7.56 $\pm$ 0.27	0.89 $\pm$ 0.05
	1	6.98 $\pm$ 0.65	0.91 $\pm$ 0.03
	10	6.81 $\pm$ 0.67	0.91 $\pm$ 0.08
	100	3.89 $\pm$ 0.40	0.56 $\pm$ 0.08
#9	0	7.71 $\pm$ 1.05	0.94 $\pm$ 0.10
	1	7.39 $\pm$ 0.45	0.92 $\pm$ 0.10
	10	6.29 $\pm$ 0.67	0.82 $\pm$ 0.04
	100	4.61 $\pm$ 0.65	0.65 $\pm$ 0.09
#10	0	6.82 $\pm$ 0.42	0.82 $\pm$ 0.08
	1	6.62 $\pm$ 0.68	0.80 $\pm$ 0.18
	10	3.95 $\pm$ 0.40	0.42 $\pm$ 0.12
	100	0.00	0.00



Table 35 continued

#11	0	6.25	+	0.50		0.76	+	0.08
	1	5.75	$\overline{+}$	0.22		0.75	$\overline{+}$	0.04
	10	4.91	$\overline{+}$	0.63		0.71	$\overline{+}$	0.04
	100	2.18	$\overline{+}$	0.22		0.36	$\overline{+}$	0.04

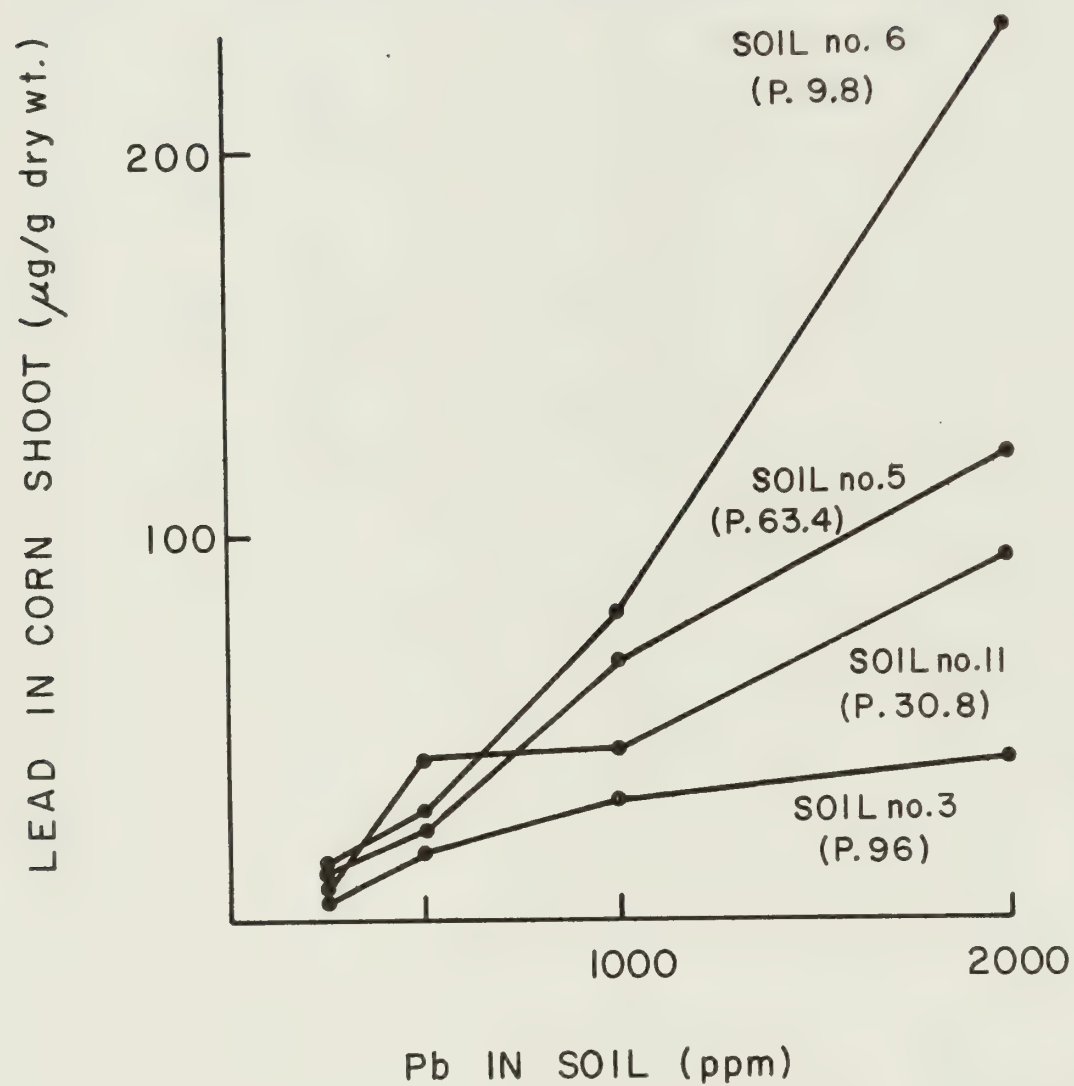


Figure 49. The Effect of Varying Phosphorous Levels on the Uptake of Lead by Corn

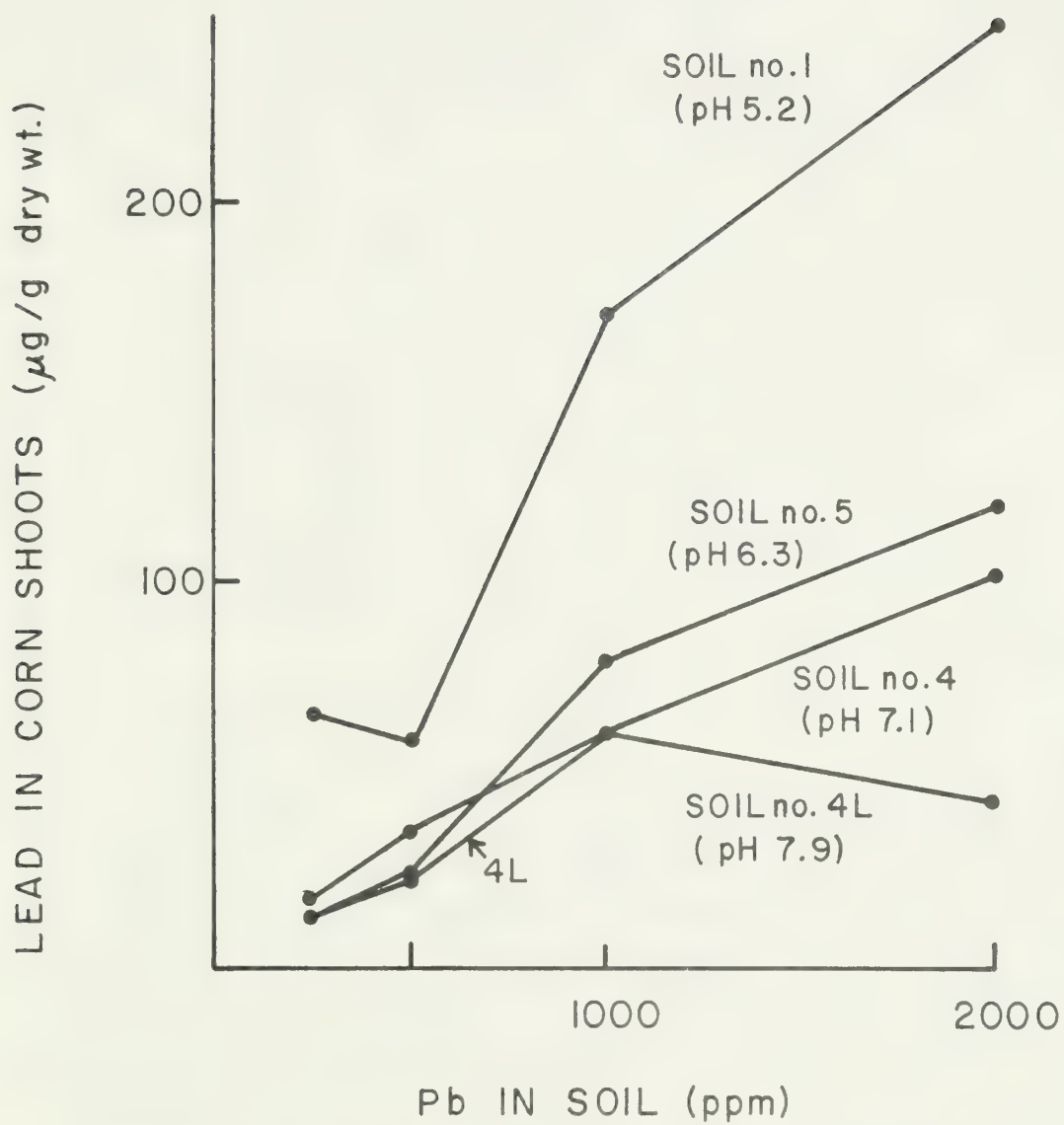


Figure 5. The effect of varying pH on the uptake of lead by corn.

duced the greatest variance in the uptake of lead (Figure 51). Soils with a low cation exchange capacity took up over 100 times as much lead as did plants grown on a soil with a high cation exchange capacity.

An additional problem became apparent after this initial Pb experiment. The higher levels of Pb caused a significant decrease in soil pH, especially in the low CEC soils. This is probably the result of removal of  $H^+$  from the exchange complex by Pb, and release of  $H^+$  upon precipitation of lead phosphates. The largest pH shift was a drop of 1.2 pH units in soil #10 with 2000 ppm Pb. In the other soils, with the exception of the acid soil (#1) which did not change, the pH was reduced about 0.5 of a pH unit by 2000 ppm Pb. In the second Pb experiment, the soil pH will be maintained by addition of  $CaCO_3$ .

Symptoms of phosphate deficiency appeared on the plants in which a significant growth depression was observed. In addition, root development and the frequency of seed germination seemed to be depressed at higher lead concentrations.

The results with cadmium were somewhat more conclusive. The fresh and dry weights of the corn shoots were reduced by 100 ppm Cd in all of the soils tested and 10 ppm Cd was inhibitory in at least two of the soils. The fresh weight

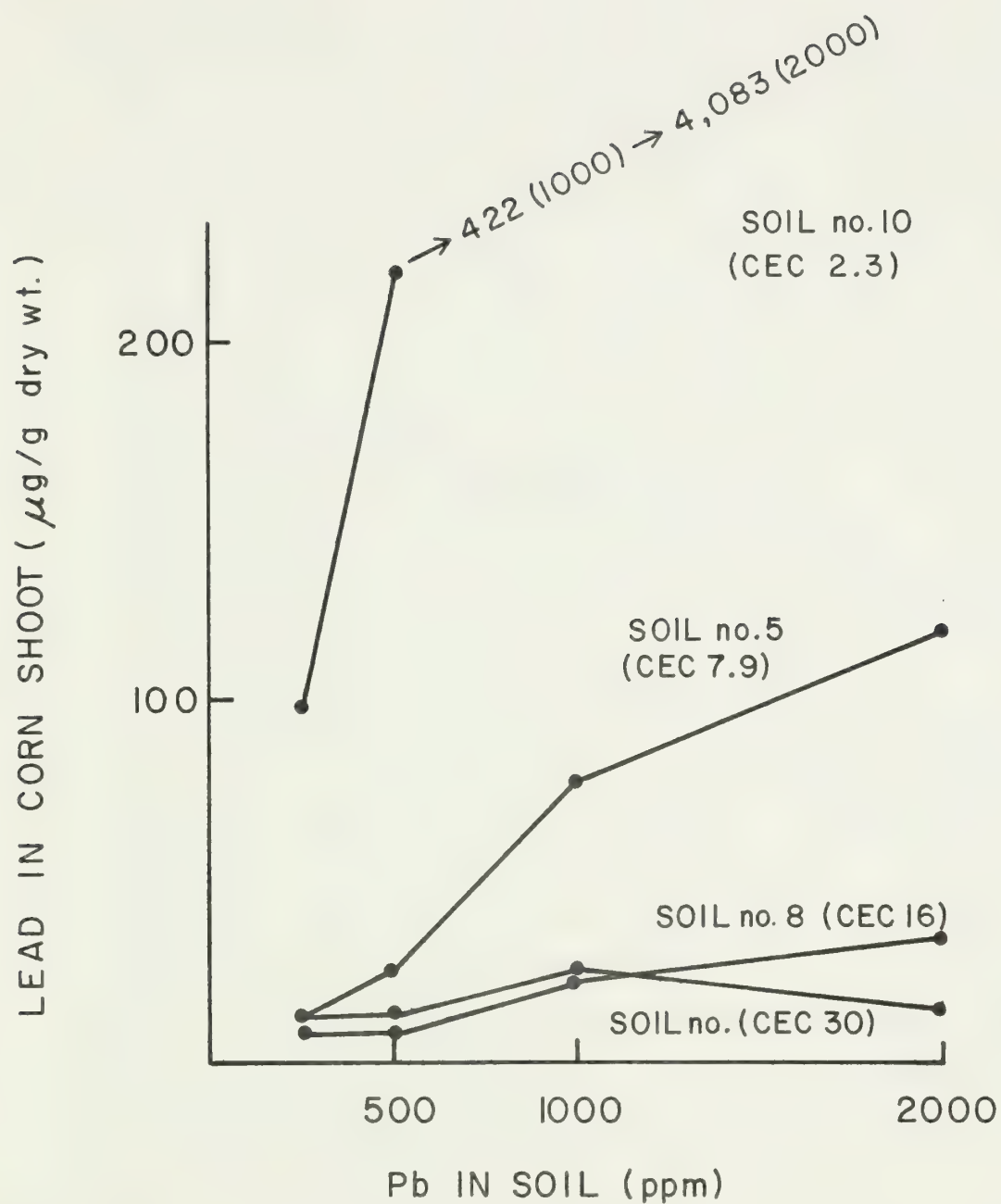


Figure 51. The Effect of Cation Exchange Capacity on the Uptake of Lead.

of the shoots was more consistently reduced than the dry weights. As with Pb, the plants grown in the acid soil and the low CEC soil showed the greatest reduction due to Cd. Figure 52 illustrates the Cd affected reduction of growth in soils of differing CEC. At 100 ppm Cd the relative reduction of fresh weight was greatest in the lower CEC soils. In Figure 53 a similar trend was observed for soil pH, although the relative differences were less. No pattern was observed for the various soil phosphate levels, although with Cd little influence of phosphate was expected. The only visual symptoms associated with the cadmium toxicity in corn shoots was a general chlorosis throughout the plant and necrosis of older leaves. Root growth and frequency of seed germination was also impaired at 100 ppm and occasionally at 10 ppm Cd.

No data on the soybeans grown in the same experimental situations are yet available. The germination of soybeans in the first lead experiment was extremely poor and the experiment must be repeated. The initial Cd-soybean experiment is presently underway and definite growth reduction, toxicity symptoms, and reduction of germination are evident. The symptoms of Cd toxicity on soybeans appear as a characteristic browning of the main veins, pulvinus, and abscission



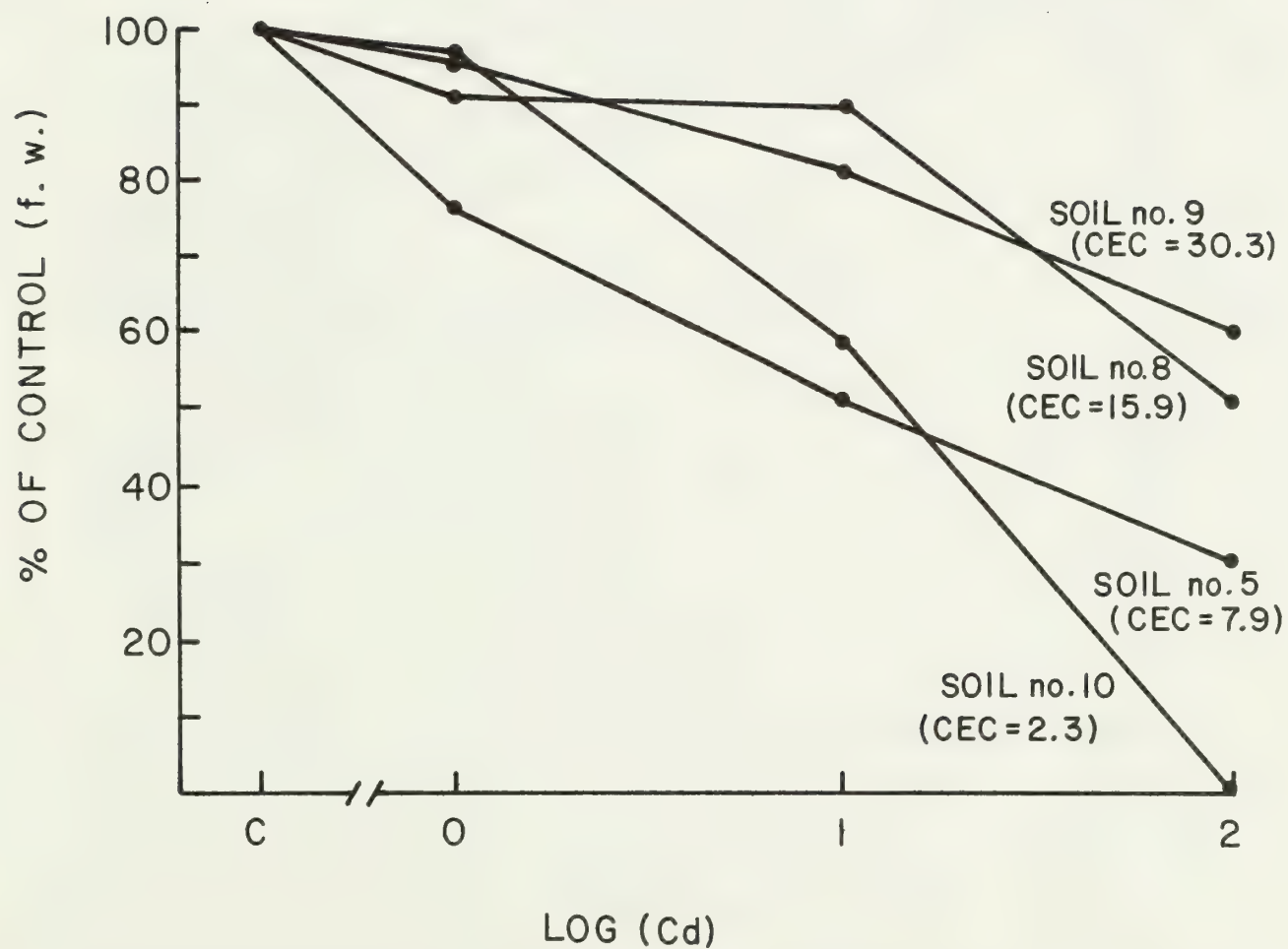


Figure 52. Influence of Cadmium on Fresh Weight of 4-week Old Corn Shoots as a Function of Soil Cation Exchange Capacity (CEC).

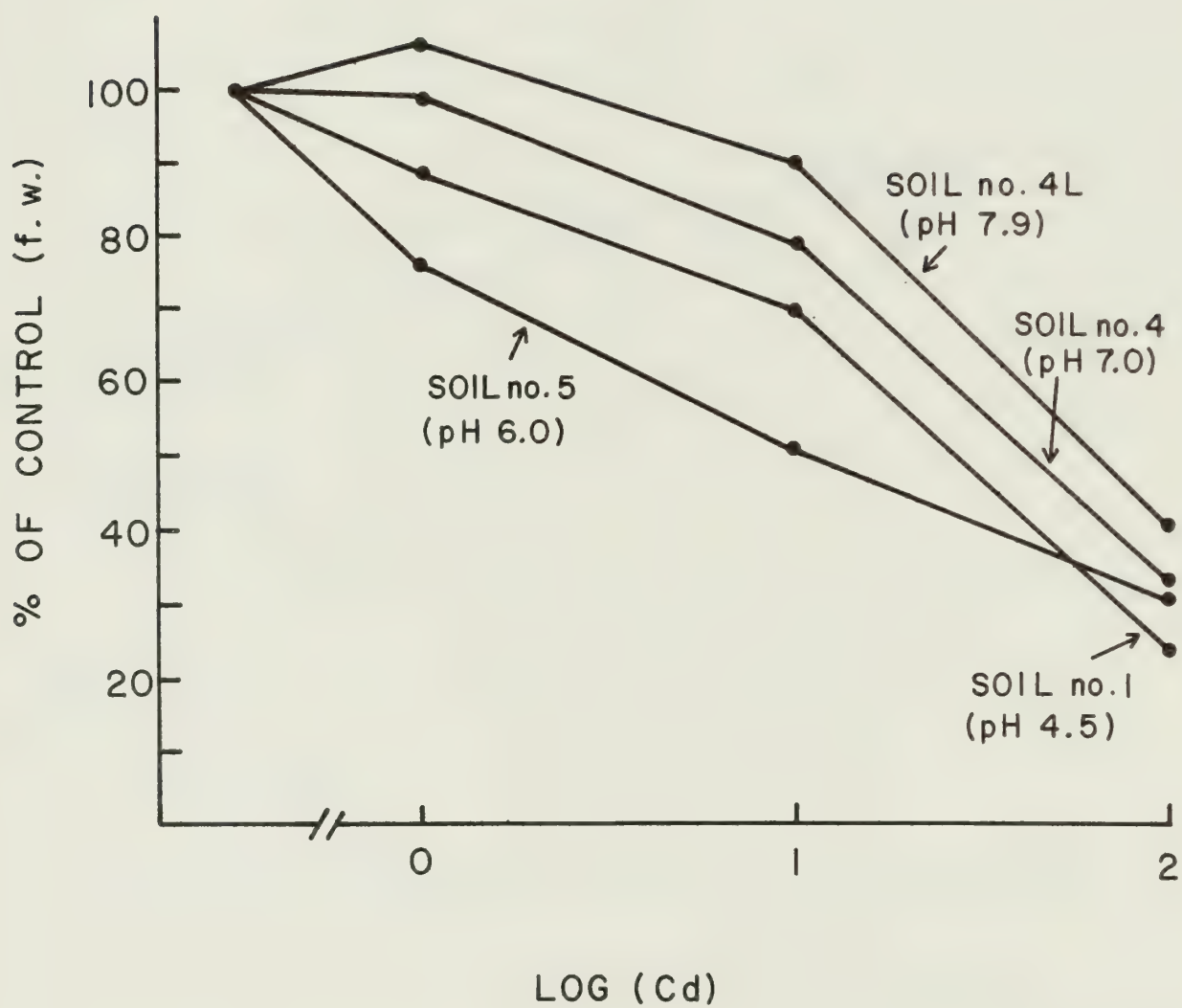


Figure 53. Influence of Cadmium on Fresh Weight of 4-week Old Corn Shoots as a Function of Soil pH.

zone of the petiole. In addition, young leaves become chlorotic and stem growth is impaired giving a rosette appearance. The symptoms are apparent in several cases at 1 ppm Cd.

A classic example of cadmium induced chlorosis is shown in Figure 55. These leaves are the second trifoliate from soybean plants grown hydroponically in the indicated cadmium concentrations for 2 and one-half days.

While corn roots were sensitive to very low levels of Cd, corn leaves showed no chlorosis below several ppm treatment level (Figure 54). This response was pH sensitive being most pronounced at acidic pH's and least pronounced at neutral pH.

#### Effects of Lead on Root Elongation (PRD-107)

In view of the effects of lead on root growth mentioned previously, a preliminary experiment was done. Corn (Zea mays L., Wf9xM64) was germinated in the presence of  $\text{PbCl}_2$  at the concentrations indicated in Figure 51. The controls contained  $\text{MgCl}_2$  at equimolar concentrations as a check for osmotic effects. The seeds were germinated on filter paper in petri dishes saturated with 10 ml of the solutions containing Pb or Mg. At 4 days all of the seeds had germinated but elongation of the radicle was significantly inhibited by 100 to 250 ppm Pb and nearly eliminated by 500 ppm Pb.

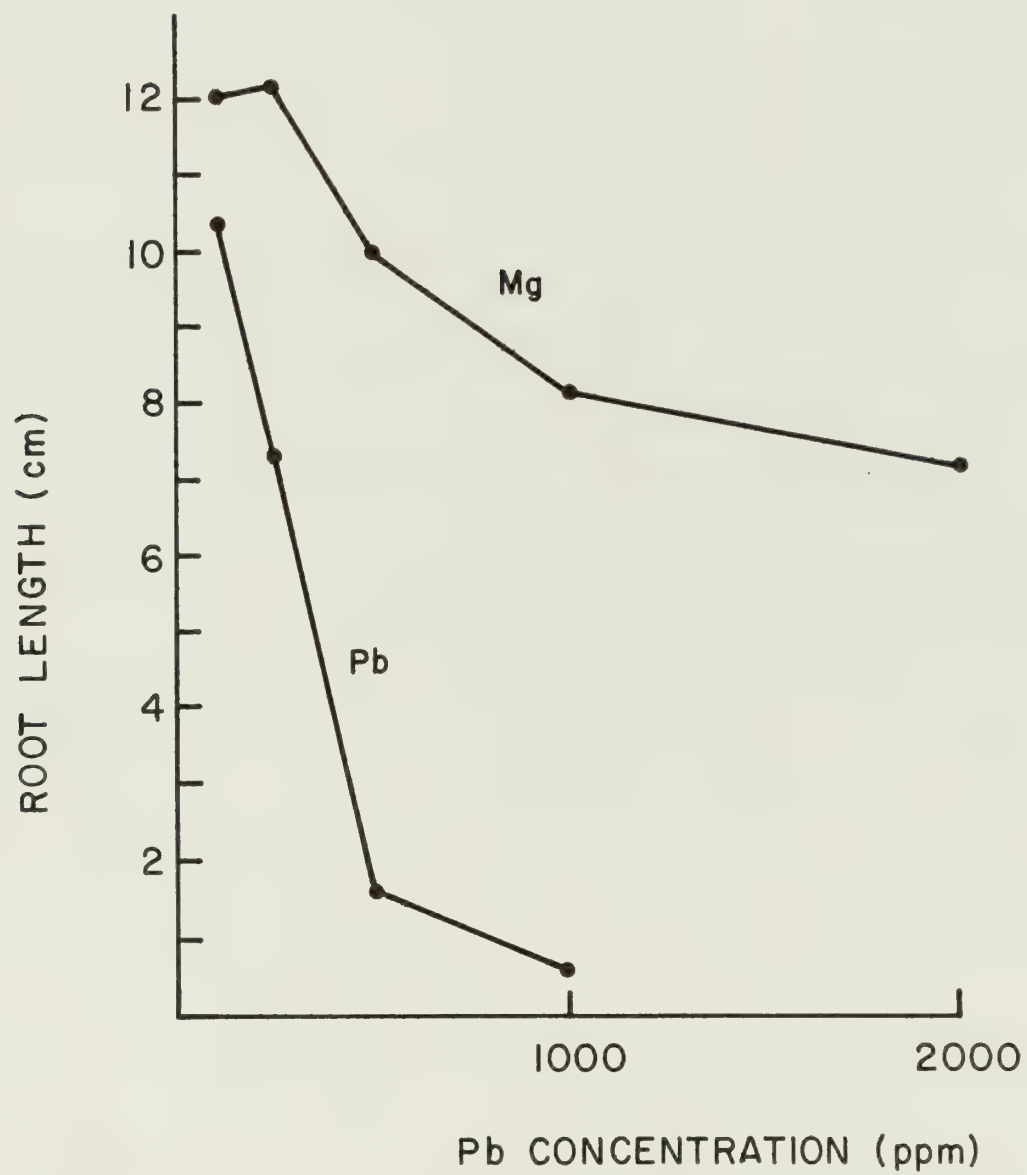


Figure 54. The Influence of Pb on Elongation of Corn Roots.

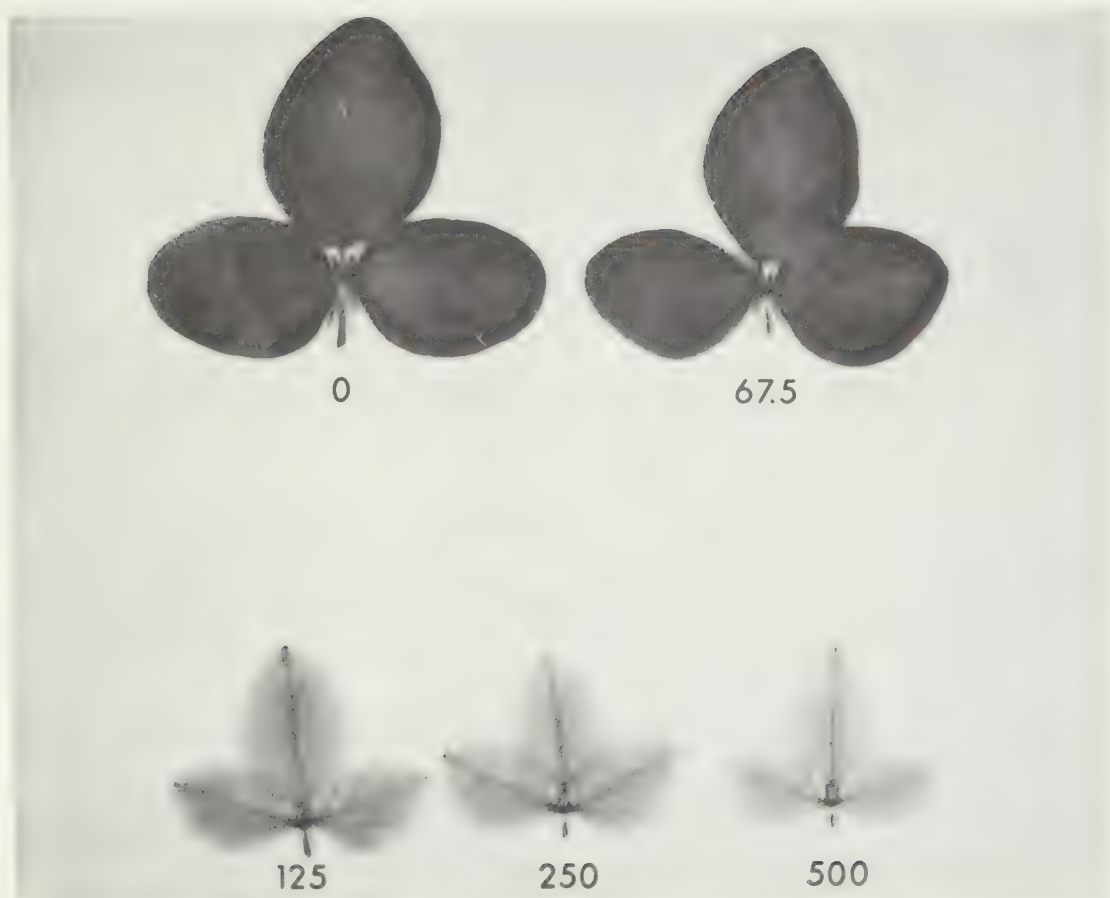


Figure 55. Second trifoliate of soybean plants treated with  $\text{Cd}^{++}$  in hydroponic solution. Numbers indicate the number of micrograms  $\text{Cd}^{++}$ /liter as  $\text{CdCl}_2$ . Chlorosis and reduction of leaf size become apparent at 125  $\mu\text{g}/\text{l}$ .

The controls showed an osmotic effect on root elongation but the Pb effect was much more pronounced. The effect of lead on root elongation is pronounced enough at low concentrations that further experiments should be done in soil.

Experimentation has been initiated concerning the effects of Pb and Cd on root elongation in soil systems. Figure 56 illustrates the Pb effect on elongation of corn roots in a loamy sand, 5 days after planting. Each data point is the mean of 20 determinations. A series of controls were also run with  $\text{MgCl}_2$  at equimolar concentrations to the  $\text{PbCl}_2$  treatments to illustrate that the lead inhibition is not totally osmotic. The Pb inhibition becomes quite significant between 250 and 500 ppm Pb. Further studies are being pursued using a variety of soils and species.



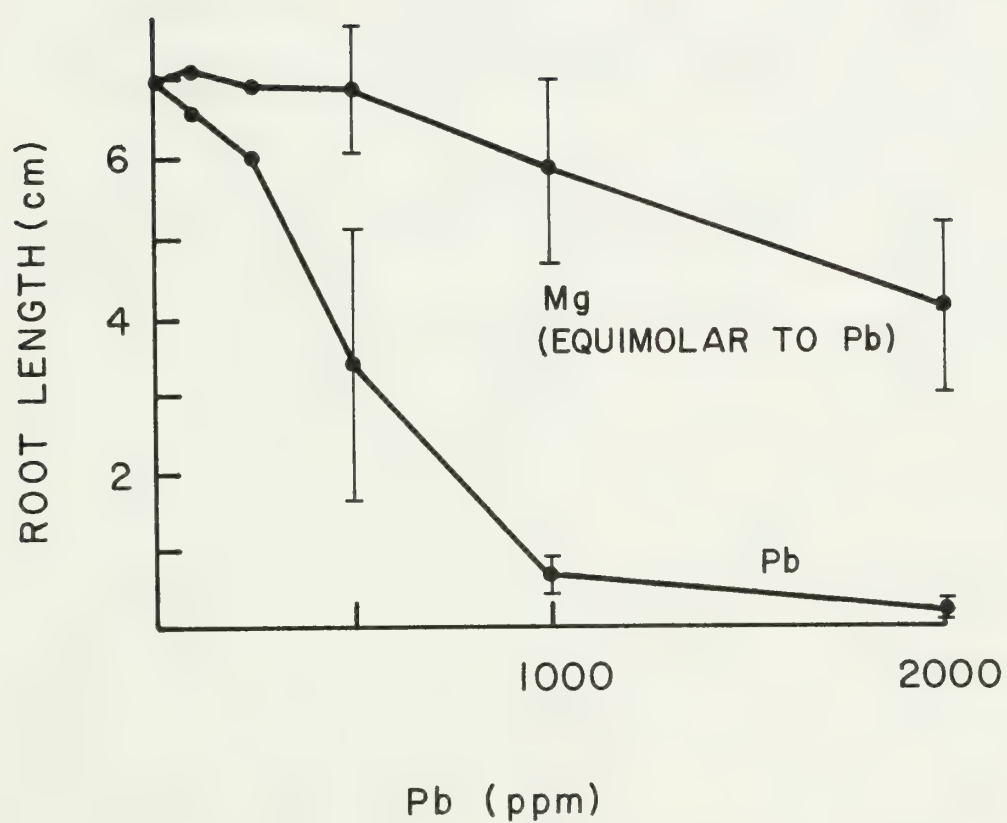


Figure 56. Effect of Pb on Elongation of Corn Roots in Bloomfield Sand.

#### D. Lead Deposition in Corn

##### Background

In the last progress report, we indicated that there were a number of large lead deposits on the interior of hydroponically grown corn roots. At that time we indicated that we did not know whether or not those deposits formed as a result of lead leaking into the root through the cortex that was damaged when lateral roots formed. We have since demonstrated that these interior lead deposits are formed by a cellular organelle in the following sequence (Figures 57-65).

Within two hours after the introduction of lead, regardless of the chelating agent, dense deposits appeared in dictyosome vesicles throughout the root. Not all of a dictyosome's vesicles contained the deposits. Deposits were more frequent toward the secreting face than the forming face, although some were observed on the forming face. Hypertrophied dictyosomes of the root cap contained fewer deposits than the more normal dictyosomes toward the center of the root. However, some secretion products of the hypertrophied vesicles that had passed through the plasmalemma did contain many dense deposits. Vesicles containing lead deposits were never observed fusing with one another.

Figures 57-61. Electron micrographs of corn roots treated with Pb. Figure 57. Root tip one hour after introduction of Pb. Note dense deposits in dictyosomes vesicles (arrows). Figure 58. Higher magnification view of Figure 57. Figure 59. Older deposit of Pb in corn root. Figure 60. Dictysome vesicles (arrows) depositing cell wall material. Figure 61. Typical deposit surrounded by membrane (arrow).

Figure 57

Figure 58

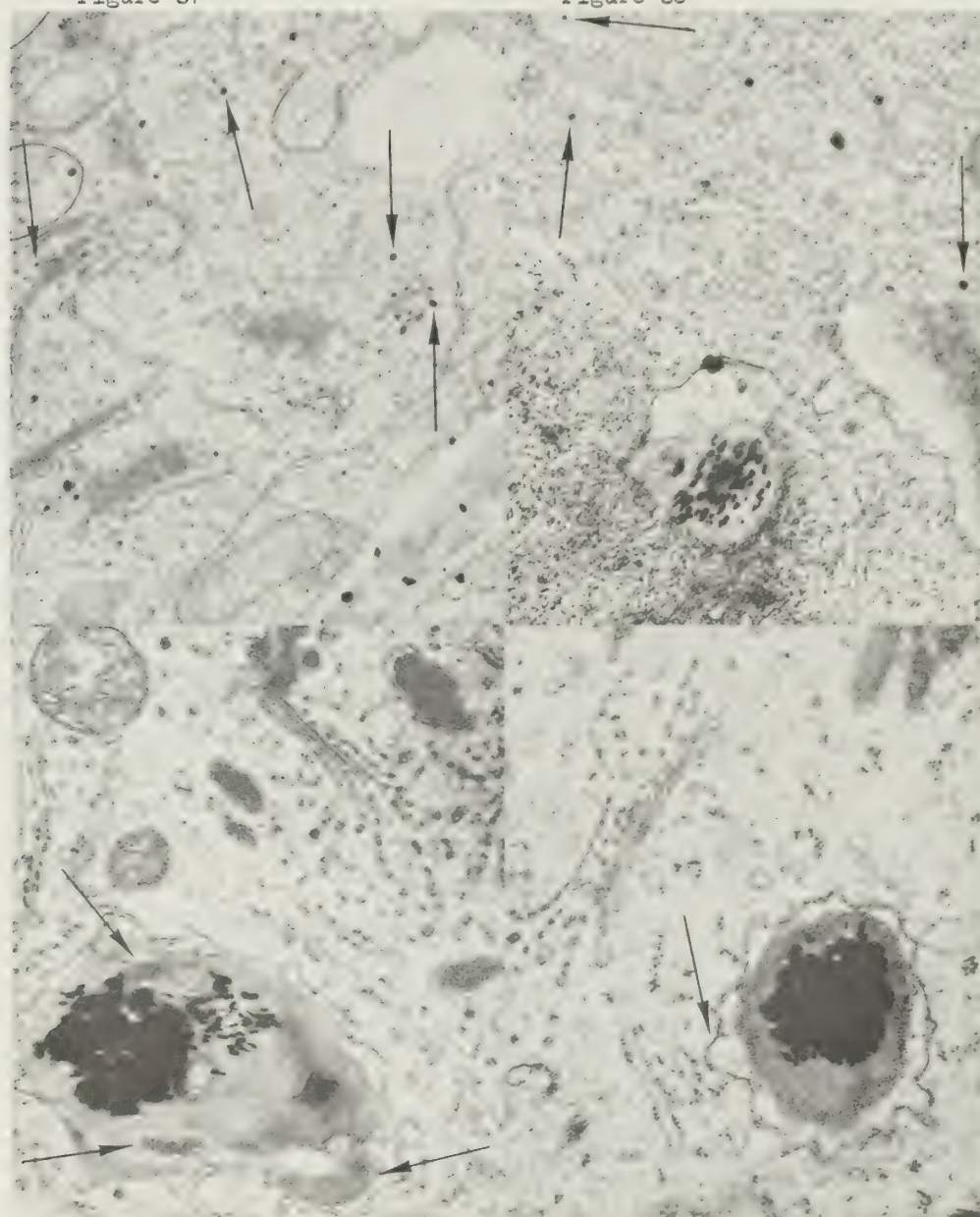


Figure 60

Figure 61

Figures 62-65 Electron micrographs of corn roots treated with Pb. Figure 62. Deposit moving to periphery of cell. Figure 63. Plasmalemma and membrane surrounding deposit fuse. Figure 64. Cell wall and cell wall material around deposit fuse. Figure 65. Typical appearance of deposits in cell walls.



Figure 62

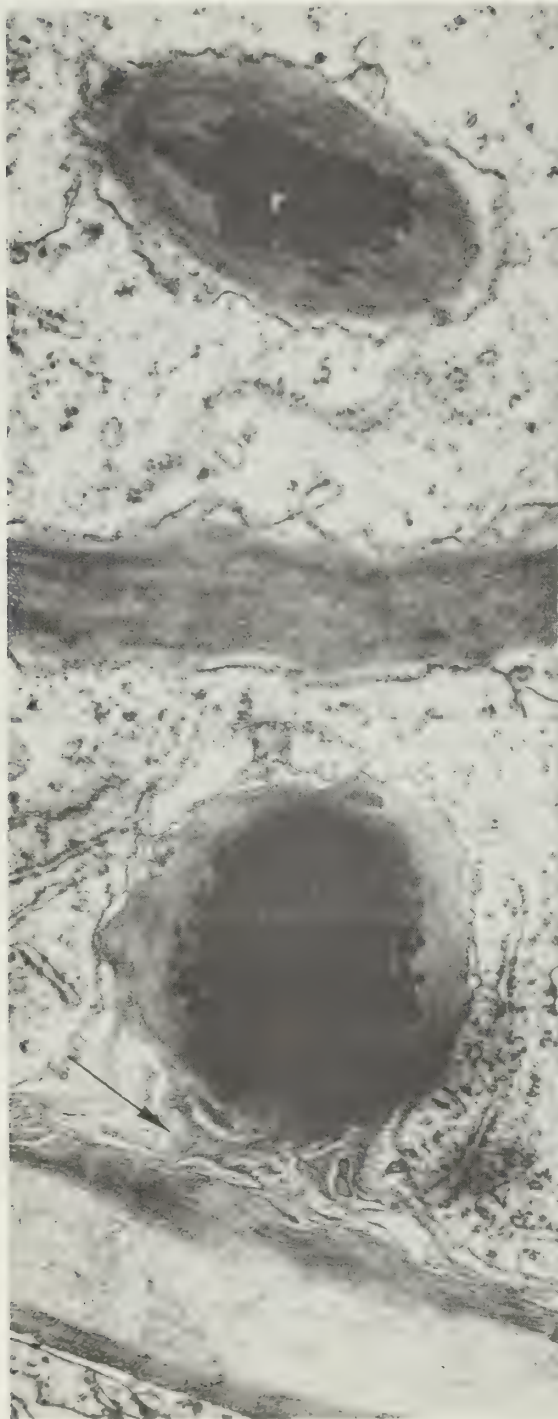


Figure 63

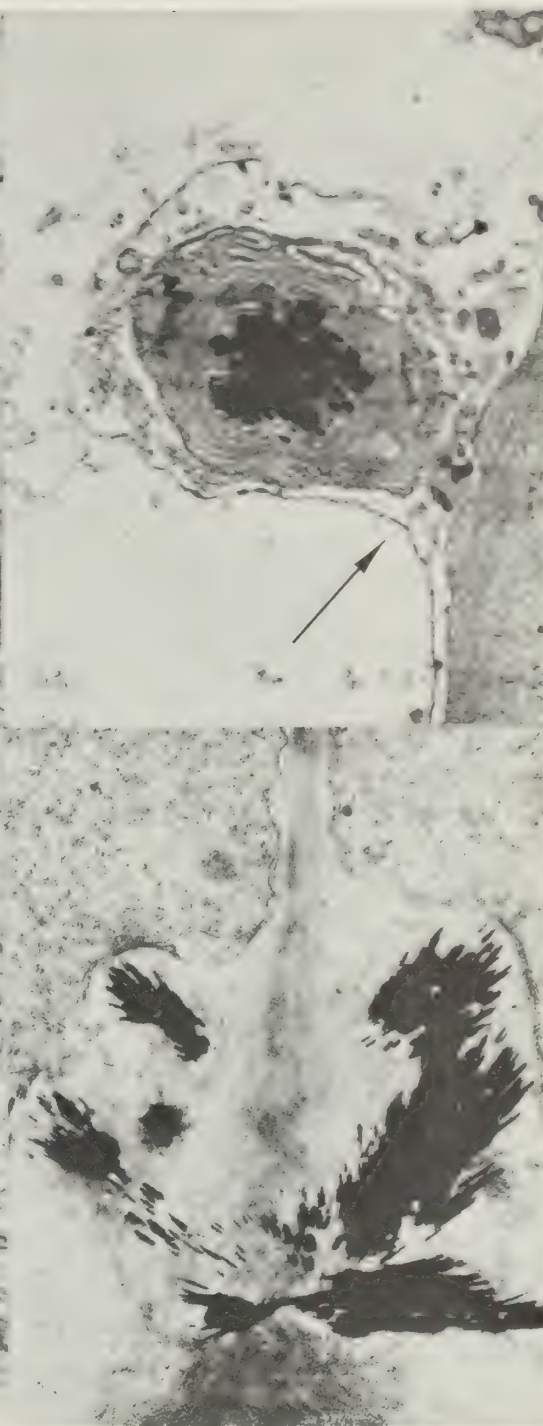


Figure 64

Figure 65



After longer exposure to lead, the deposits became larger. These larger deposits consisted of a group of crystals encased in what appeared to be cell wall material and surrounded by a unit membrane. Dictyosome vesicles containing cell wall precursors were observed fusing with the deposits. The usual size of the deposits was 1 to 2  $\mu$  wide by 3 to 5  $\mu$  long.

Larger deposits were observed in the periphery of cells where the membrane surrounding the deposit fused with the plasmalemma. Subsequently, the cell wall material surrounding the deposit fused with the cell wall. The cell wall at the site where a crystal had been deposited was abnormally thick due to the extra cell wall material that had been deposited with the crystal. Often the cell wall and the crystal protruded some distance into the cell. These crystalline deposits were clearly visible with the light microscope and often tended to be opposite one another in adjacent cells.

Crystals with similar morphology and associated with uneven, protruding cell walls were observed throughout the root system, in stems, and in leaves of corn plants. In the roots the crystals were most prevalent in, but not limited to, the stele, while in the stems and leaves they

tended to be in or close to vascular bundles. More crystals were present in roots than in stems, and stems contained more crystals than did leaves. Crystals were observed to be associated with every cell type except phloem sieve tube and companion cells and epidermal guard and accessory cells. Crystals were observed with treatment levels as low as 10 ppm. While the frequency of deposit occurrence increased with increasing lead levels, crystal morphology, method of deposition, and final location in the cell remained constant.

Preliminary work on localizing lead in soil grown plants is underway. At very high lead levels (3000  $\mu\text{g}/100$  g soil) cell wall deposits (similar to those in hydroponic culture) are present. At lower lead levels (250  $\mu\text{g}/1000$  g soil) dense deposits are associated with mitochondria, plastids, and some membranes. The in vivo mitochondrial deposits are very similar to those found when in vitro mitochondria were treated with  $\text{PbCl}_2$  (Figures 66-68).

Figures 66-68. Transmission electron micrographs of corn mitochondria. Figure 66. In vitro mitochondria treated with  $\text{PbCl}_2$ . Pb deposits show up as dense deposits. No heavy metals used in specimen preparation. Figure 67. Pb deposits in in vitro mitochondrion. Heavy metals used in specimen preparation. Figure 68. Dense deposits in mitochondrion of corn root grown in Drummer soil amended with 250 ppm Pb. Whether these dense deposits are lead or an artifact ppt is unknown at this time.



Figure 66

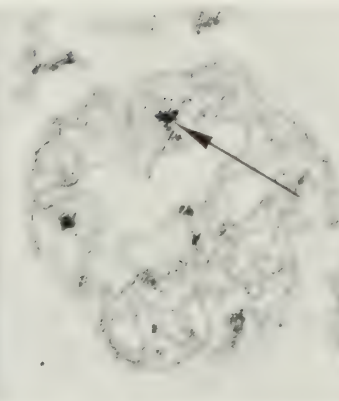


Figure 67

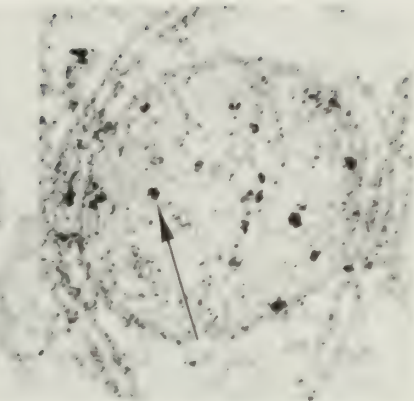


Figure 68

E. The Effect of Cadmium on the Iron and Zinc Balance  
in Hydroponically Grown Corn (PRD 110, 104, 107)

Background

Cadmium is among those trace metals with which there has been an increased concern because of its increasing environmental distribution. It has been shown to be taken up by and to be toxic to plants (6, 7, 8, 10, and 13).

Although the toxicity of Cd to plants has received recent attention, little is known about how Cd affects the physiology of plants. The gross effects of Cd toxicity have been shown to be chlorosis, necrosis and reduction in growth (10, 13, 6, 8, and 11). Root, Koeppe and Miller (1973) have further shown that Cd stimulated  $O_2$  uptake in corn roots at low Cd concentrations but was inhibitory at higher Cd concentrations. They have also shown that the ATP content of these Cd-treated corn roots was reduced to approximately half that of the control. Lagerwerff and Biersdorf (1972) and Turner (1973) have speculated that Cd may cause root damage. Haghiri (1973) has suggested that Cd toxicity resembles Fe (deficiency) chlorosis. Lagerwerff and Biersdorf (1972) have shown that Cd and Zn are competitive cations, resulting in lower Zn levels where Cd is present. Little other evidence, however, has been presented that shows if

Cd affects either directly or indirectly the nutrient balance of other essential plant nutrients. A significant change in the nutrient balance may, in part, explain one mode of Cd toxicity.

#### B. Methods and Materials

Corn plants (Zea mays L., Wf9xM14) were grown hydroponically in the greenhouse in an aerated, complete hoagland's solution maintained at pH 3.5 to 4.0. The iron was triple strength in the form of ferric citrate. At two weeks of age twelve corn seedlings were transferred into 12-liter treatment containers. The plants were treated in duplicate containers with 0, 1, 2, 5, 10, 20, and 40 ppm Cd. Cadmium was added as  $\text{CdCl}_2$  and deionized water was added daily to compensate for transpiration loss.

After 6 days of treatment the plants were harvested and the roots washed in water for 30 minutes. The roots and shoots were then oven dried at  $105^\circ\text{C}$ , weighed, dry-ashed at  $450^\circ\text{C}$  overnight, dissolved in 3N HCl and analyzed for Cd, Fe and Zn using atomic absorption spectroscopy.

The chlorophyll content of the leaves was measured by punching leaf discs from the leaves as described by Root et al. (1973).



### C. Results and Discussion

Cadmium had the effect of decreasing the Zn content and increasing the Fe content in the roots and shoots. This effect was more pronounced in the roots than the shoots. Figure 69 shows that the Zn concentration in the roots rapidly decreased to approximately 1/3 that of the control while the Fe concentration doubled. The Zn concentration in the shoots (Figure 70) dropped abruptly, as it had in the roots, but to a lesser degree; approximately 2/3 that of the control. For both the roots and shoots a Cd solution concentration greater than 1 ppm did not significantly further decrease the Zn content. However, the Cd treatments did not affect the Fe concentrations at solution concentrations of 1 or 2 ppm Cd but did increase the Fe levels in solutions containing 5 ppm Cd and greater.

It has been suggested by Haghiri (1973) that Cd-treated plants appear to have an Fe chlorosis; a symptom of Fe deficiency. Although Cd-treated plants do possess Fe chlorosis symptoms, our results do not support the position that the Fe content has been reduced. Indeed, to the contrary, the Fe content has increased in those containing high levels of Cd. Thus it may be that Cd toxicity may be indirectly associated with the Fe and Zn balance in the plant.

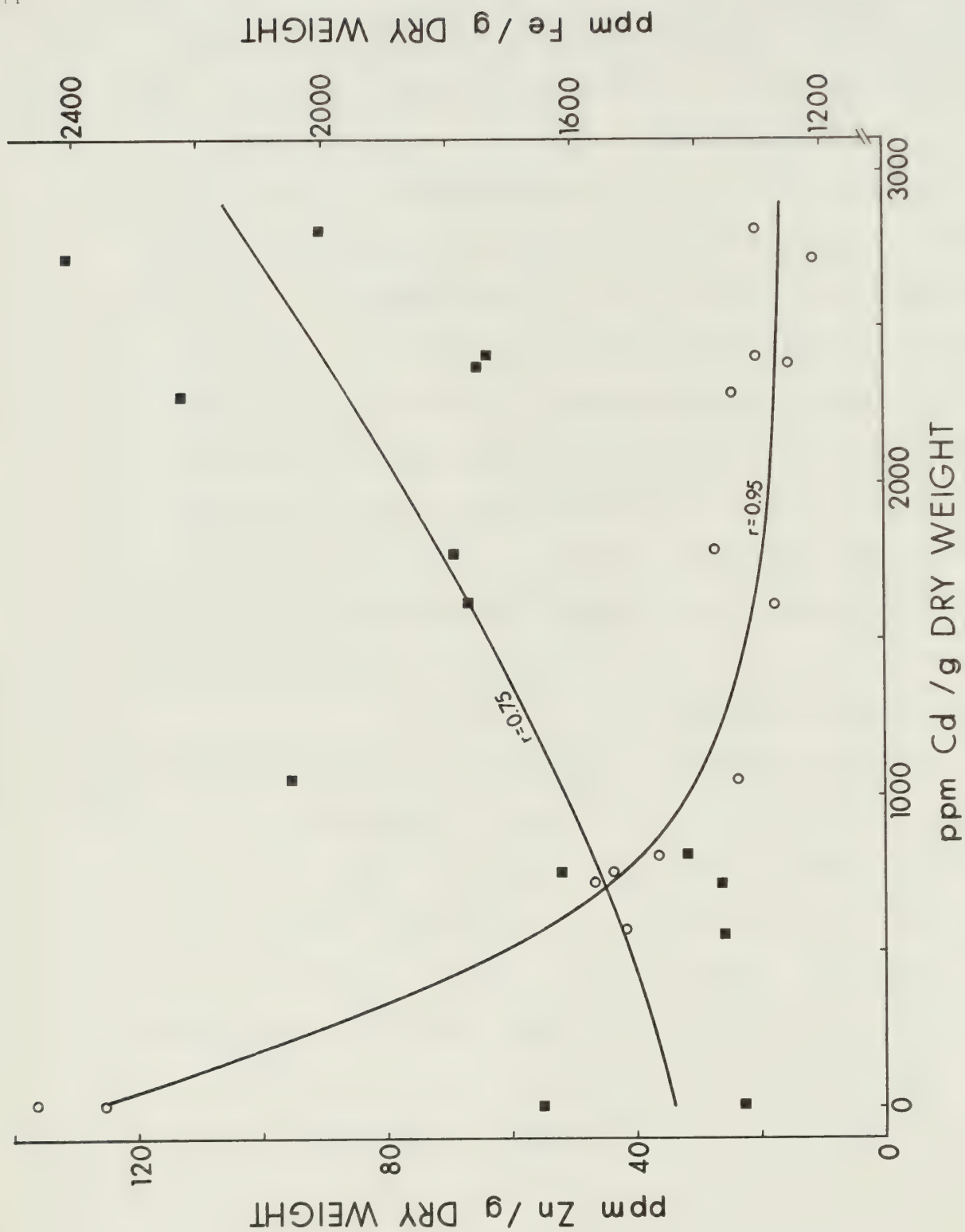


Figure 69 The effect of cadmium tissue concentration on the concentration of Fe<sup>2+</sup> and Zn<sup>2+</sup> in corn roots after 6 days of treatment. The curves represent a statistical fit using a quadratic multiple regression analysis. R values are given next to the respective curves.

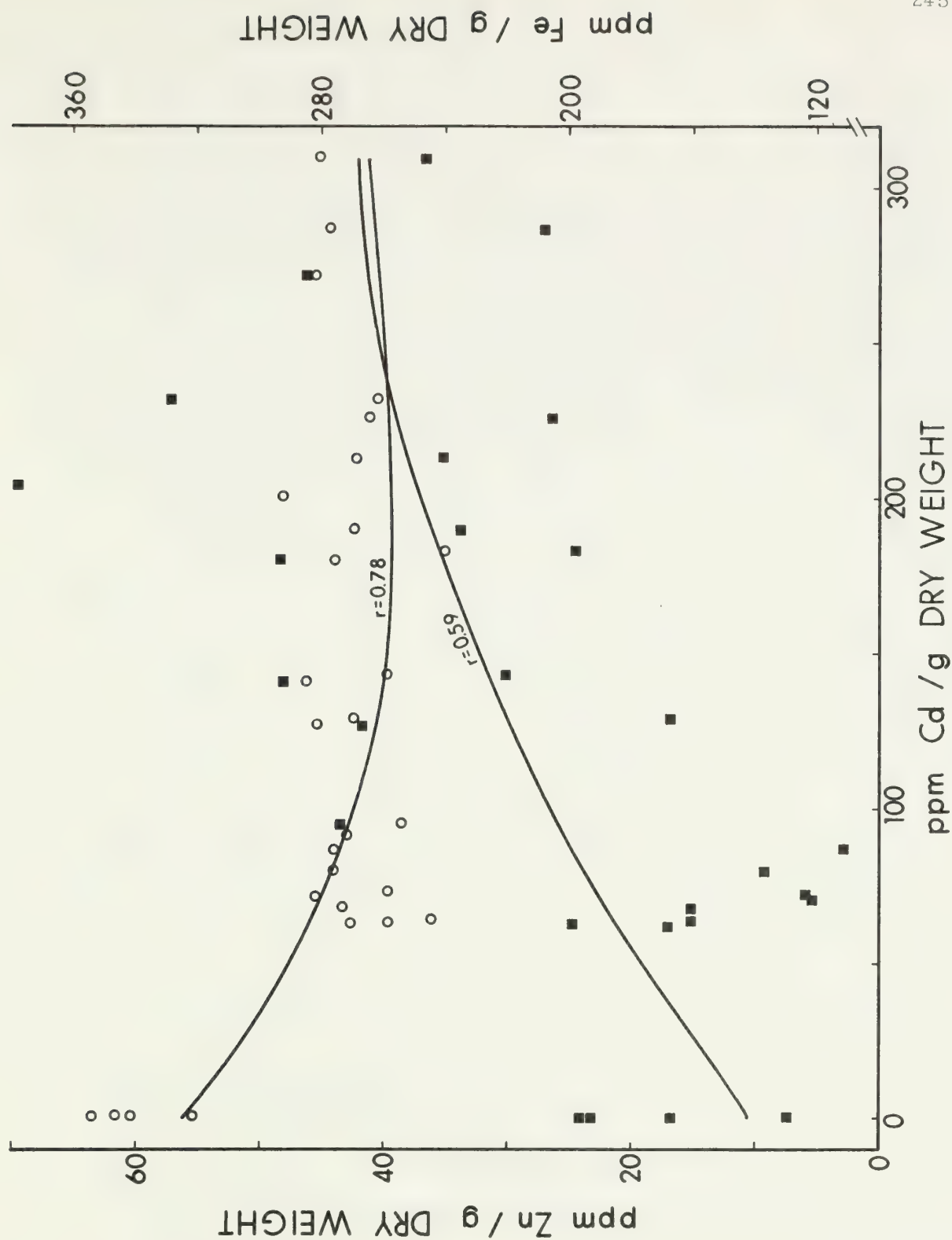


Figure 70 The effect of cadmium tissue concentration on the concentration of Fe and Zn in corn shoots after 6 days of treatment. The curves represent a statistical fit using a quadratic multiple regression analysis. R values are given next to the respective curves.

It is known that the supply of Zn is connected in some manner with the uptake and metabolic functions of Fe in plants (Olsen, 1972). Plants deficient in Zn have been shown to accumulate large quantities of Fe (Ambler and Brown, 1969; and Rosell and Ulrich, 1964). Furthermore, it has been shown that Zn deficiencies can be easily induced. For example, when Zn levels are marginal an excess application of phosphate fertilizer can induce a Zn deficiency resulting in an increase in the Fe/Zn ratio (Adriano and Murphy, 1970; Adriano et al., 1971; Ambler and Brown, 1969; Ambler et al., 1970; Caniron et al., 1969; and Warnock, 1970). The results in Figures 71 and 72 show an increase in the Fe/Zn ratios in the roots and shoots of Cd-treated plants with an increase in the Cd content. These results strongly suggest that Cd may be inducing a Zn deficiency resulting in an Fe/Zn imbalance.

Numerous investigators have reported reductions in yield with increased application of Cd. The reductions in dry weight of the roots and shoots (Figures 73 and 74) show that there is a continuous decrease in weight with Cd content and suggest that even modest Cd tissue levels may reduce yields.

Ambler and Brown (1969) have presented evidence to show that within certain limits the Fe/Zn ratio may be direct-

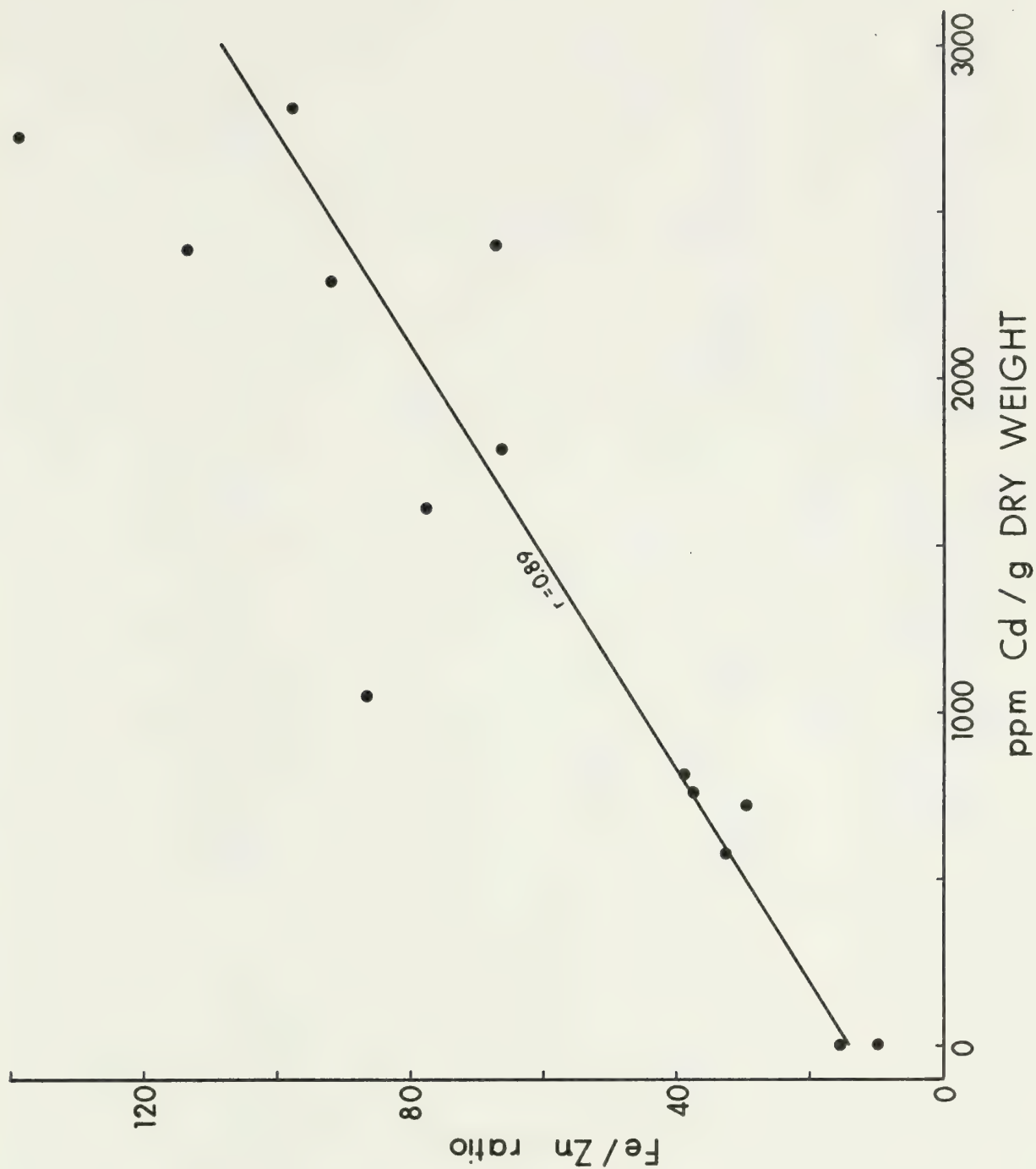
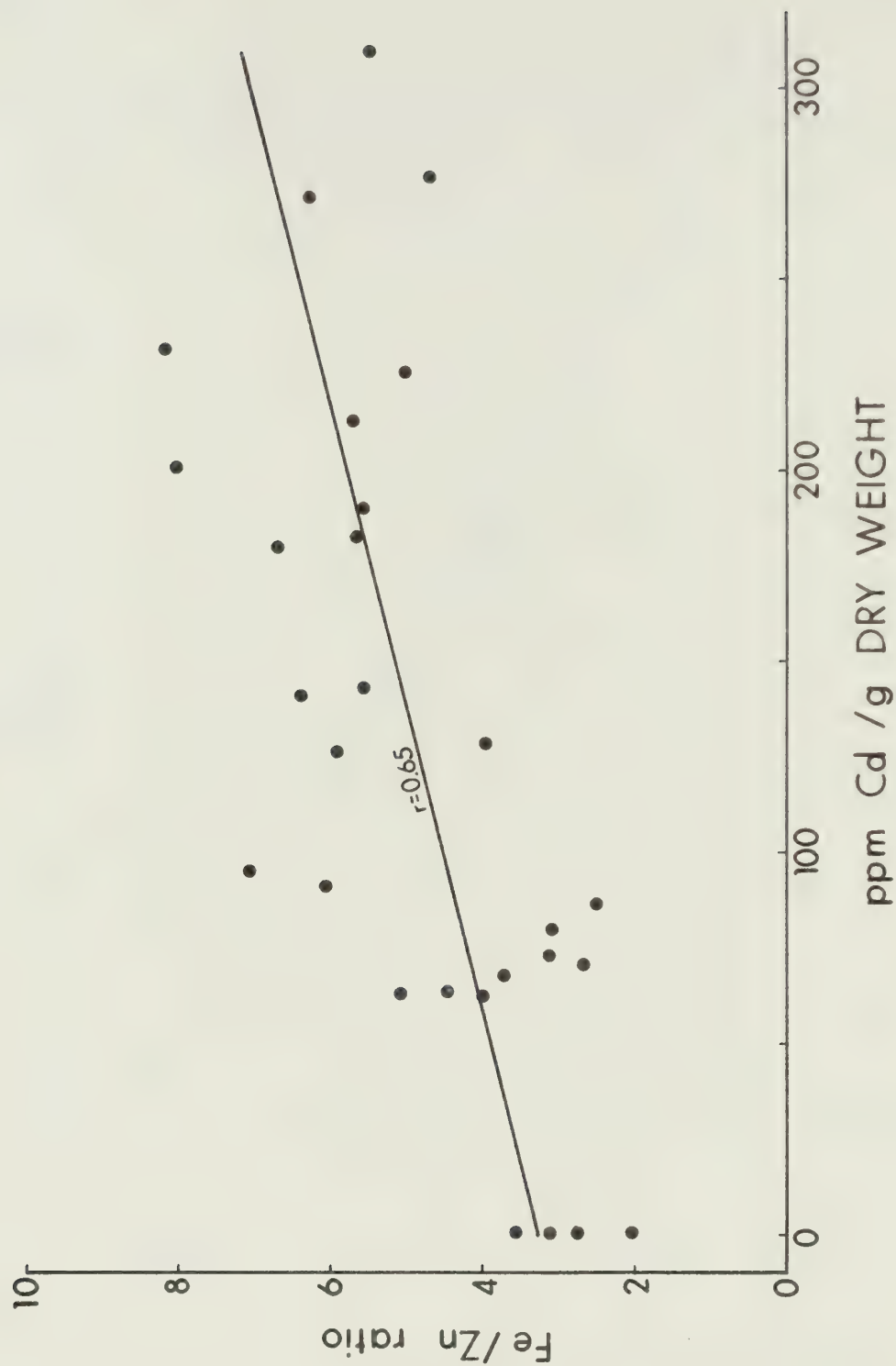


Figure 71 The effect of cadmium tissue concentration on the Fe/Zn ratio in corn roots. The line represents a statistical fit using a linear regression analysis. The  $r$  value is given next to the line.





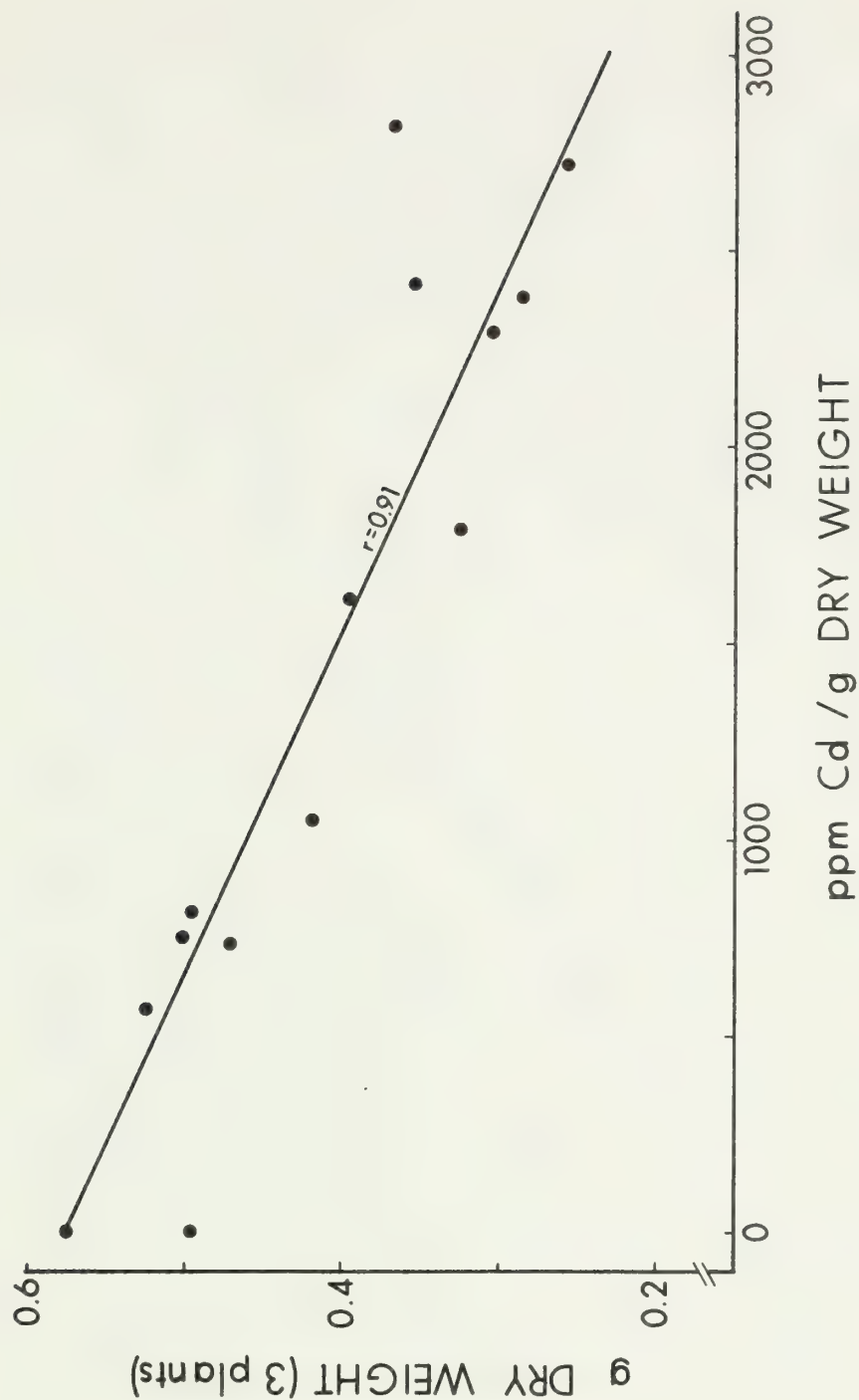


Figure 73 The effect of cadmium tissue concentration on the dry weight of corn roots after 6 days of treatment. The line represents a statistical fit using a linear regression analysis. The  $r$  value is given next to the line.

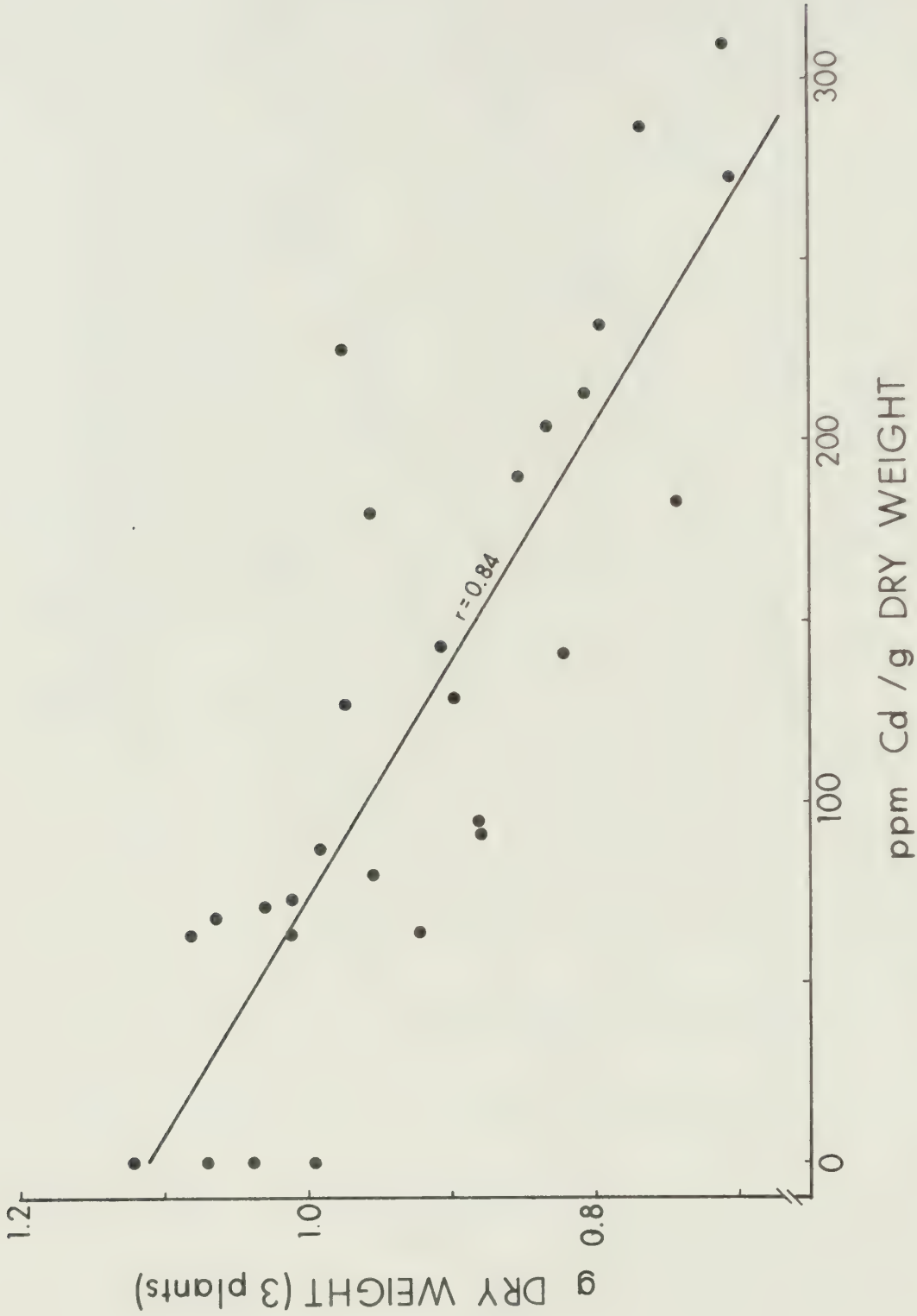


Figure 74 The effect of cadmium tissue concentration on the dry weight of corn shoots after 10 days of treatment. The line represents a statistical fit using a linear regression analysis. The  $r$  value is given next to the line.

ly related to yield. Figures 75 and 76 showing a correlation between Fe/Zn ratio and dry weight. A Cd-induced Zn deficiency, resulting in higher Fe/Zn ratios may be responsible for reductions in dry weight.

Chlorosis is a symptom for many plant diseases and nutrient imbalances. The amount of chlorosis found in Cd-treated plants was not found to correlate with the Cd content within the plant. As reported previously (Root, Koeppel, and Miller, 1973), the amount of Cd found in corn shoots was greater in the older leaves and less in the younger leaves. An analysis of the chlorophyll content of the leaves of Cd-treated and non-treated plants was made on a leaf by leaf basis. As shown in Figure 77 the chlorophyll content in the non-treated corn leaves was approximately uniform. In the Cd-treated plants, however, the chlorophyll content was greater in the older leaves (where the Cd content was greater) and declined approximately 50% in the younger leaves. The reduction in chlorophyll in the younger leaves where the Cd content was lower suggests that there was not a direct relationship between chlorosis and Cd content. A greater amount of chlorosis in the younger leaves does suggest the possibility of an Fe/Zn imbalance.

The data reported here suggest that Cd plant toxicity is correlated with an increase in the Fe/Zn ratio.

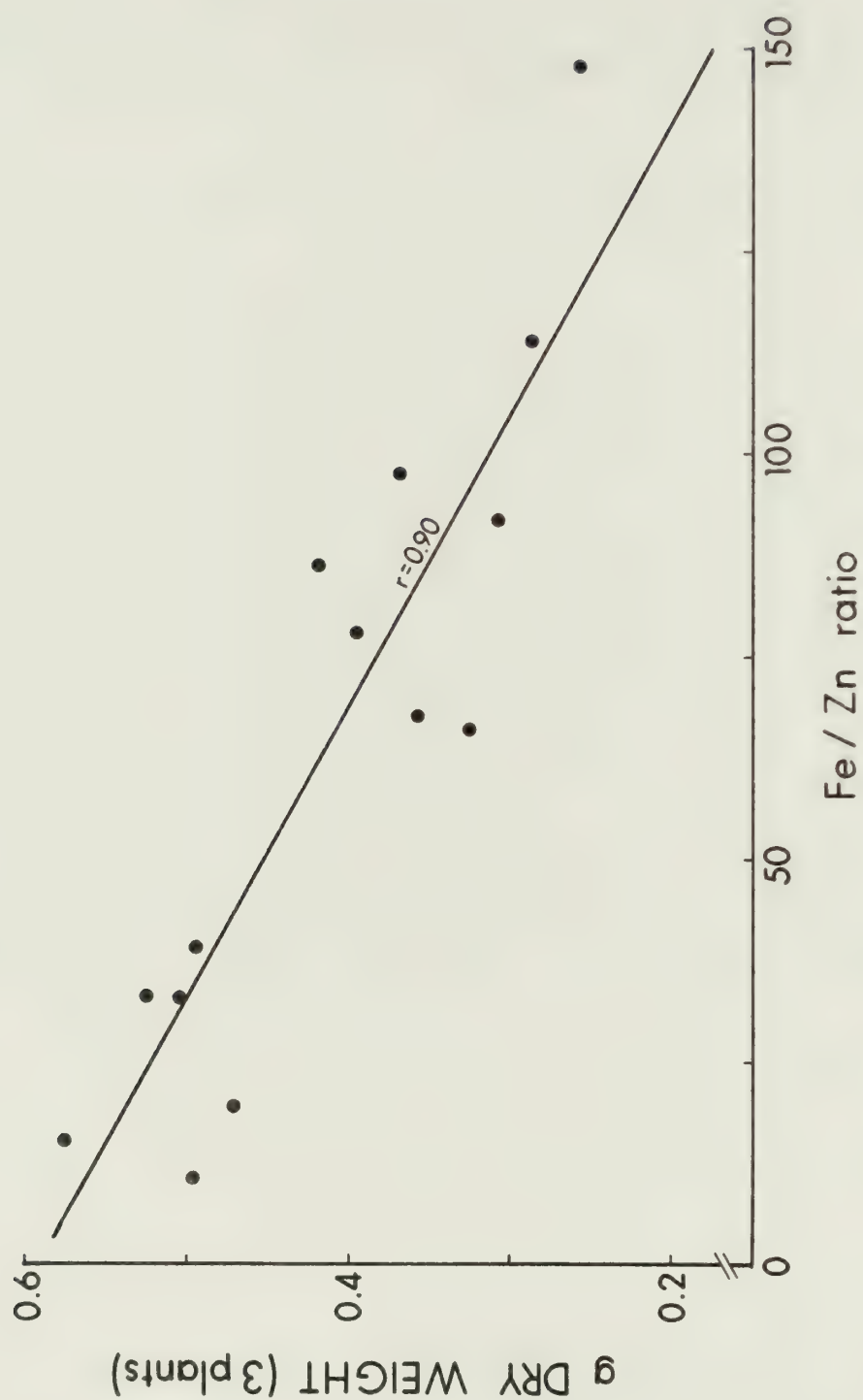


Figure 75. The effect of the Fe/Zn ratio on root weight of corn plants treated for 6 days. The line represents a statistical fit using a linear regression analysis. The  $r$  value is given next to the line.

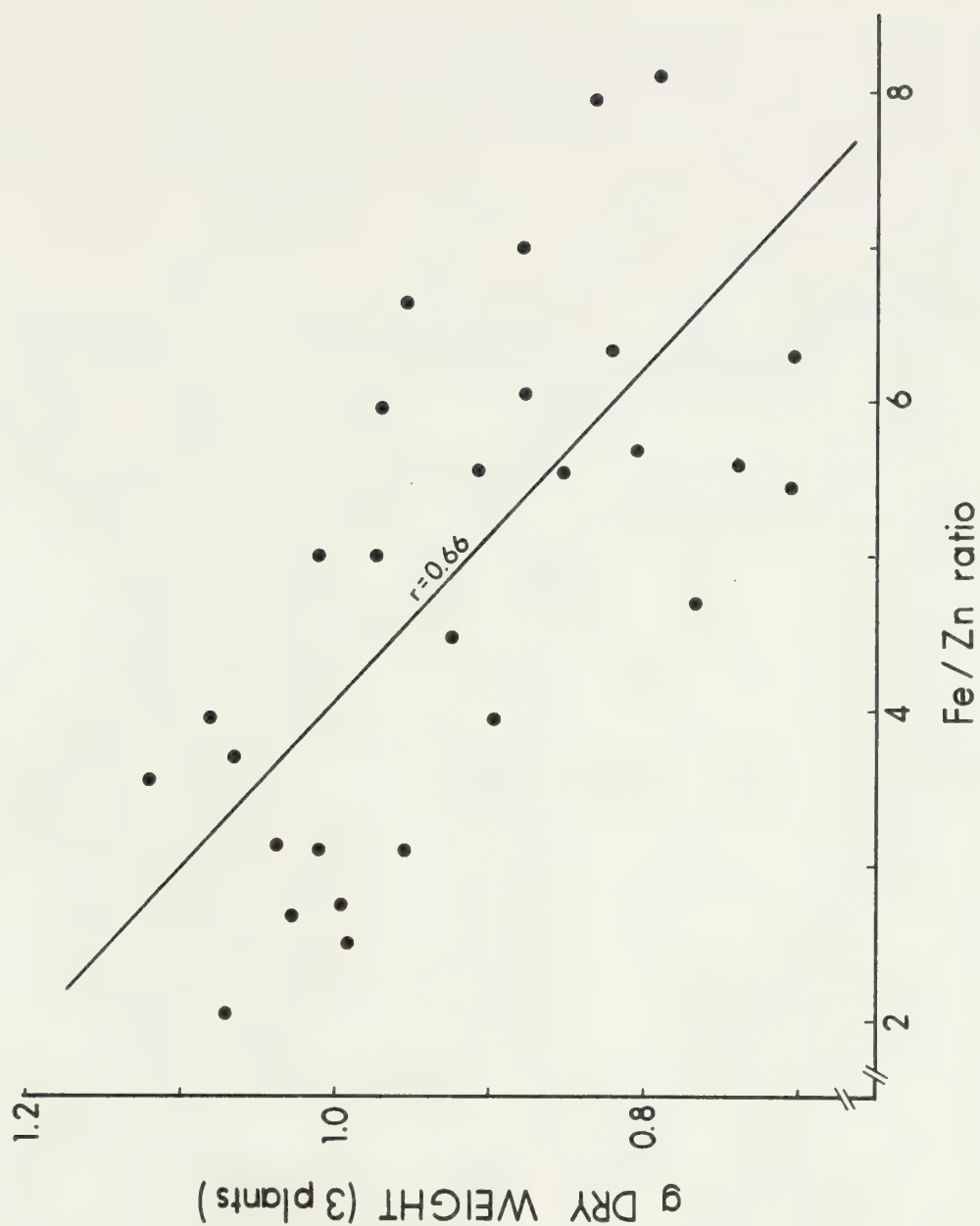


Figure 76 The effect of the Fe/Zn ratio of Cd-treated plants on the dry weight of corn shoots treated for 6 days. The line represents a statistical fit using a linear regression analysis. The  $r$  value is given next to the line.

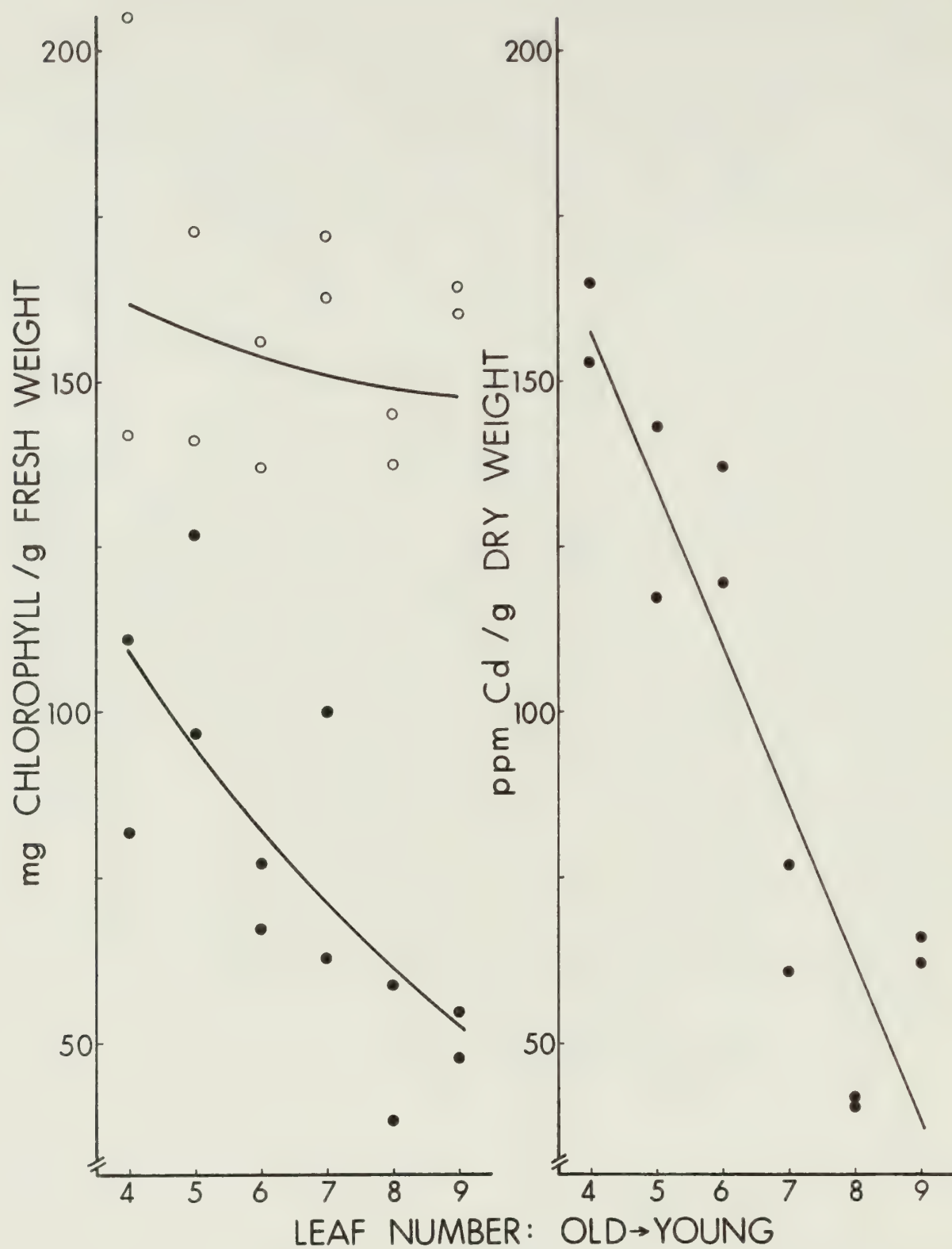


Figure 77 The effect of cadmium on the chlorophyll content of the leaves of nontreated (0) and plants treated with 1 ppm Cd (o) for 6 days. The Cd content of the leaves of the Cd-treated plants is also shown.



Although no attempt was made to determine which enzyme systems were affected; enzymes requiring Zn or Fe are likely the ones involved.

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## F. Effects on Plant Processes

### 1. Whole Plant Photosynthesis

A study was begun in the fall of 1972 in which we examined the relative toxicity of four different heavy metals to photosynthesis and transpiration. Experiments included one in which root resistance to ion uptake was removed before heavy metal treatment and the second in which root resistance was included.

In the first experiment sunflower plants were grown from seed in vermiculite and watered as needed with Hoagland Solution until they attained a height of 45-60 cm. The top 15 cm of each plant was then removed and placed in a flask of deionized water. Rates of net carbon dioxide uptake and water vapor loss were measured as described earlier (PR2--p. 240, 241; Bazzaz and Boyer, 1972), and the plant tops placed in solutions of heavy metal salts corresponding to 0, 2, 20, 100 or 200 ppm toxic ion concentration. The rate of gas exchange of each plant top was again measured on each succeeding day for a maximum of 5 additional days or until the rate of net photosynthesis dropped to less than 10 percent of the initial rate. The plant tops were then oven-dried and analyzed for heavy metal content.

At high treatment levels the rate of net photosynthesis was reduced more by Ni and Tl than Cd, and Pb was the least toxic of the four heavy metals tested (Figure 78). However, at low concentrations (2 ppm) Pb reduced net photosynthesis of sunflower to a level that was similar to that caused by Ni and lower than that observed for Cd or Tl. In general net photosynthesis decreased both with increasing treatment time and increasing treatment concentration.

When expressed as a percent of control, the rate of transpiration closely parallels the decrease in net photosynthesis for all treated plants (Figure 79). A 1:1 correspondence between transpiration and net photosynthesis was found for Pb, Ni and Tl suggesting that stomatal opening may be an important factor in the effect of these heavy metals on gas exchange. At any given leaf tissue content Cd caused a greater reduction in the rate of net photosynthesis than transpiration. This may be the result of decreased light interception since the leaves of plants treated with the higher concentrations of Cd remained turgid but became declined to the horizontal by bending down at the petiole.

A second study was completed during 1973 in which the sensitivity of sunflower was compared to that of corn

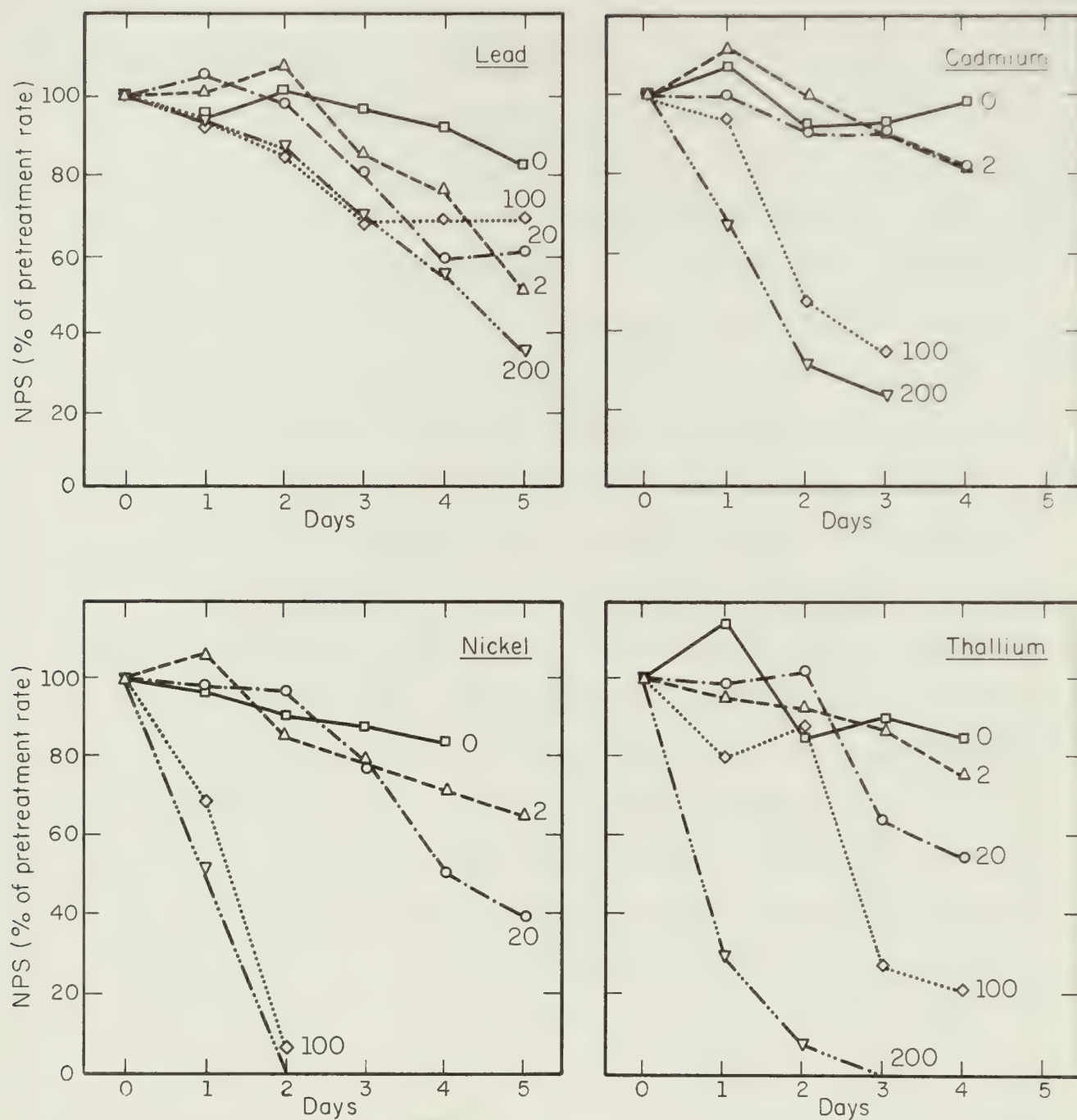


Figure 78. Rate of Net Photosynthesis (NPS) of Excised Sunflower Tops for Various Heavy Metal Ions and Different Treatment Levels (0, 2, 20, 100, 200 ppm).



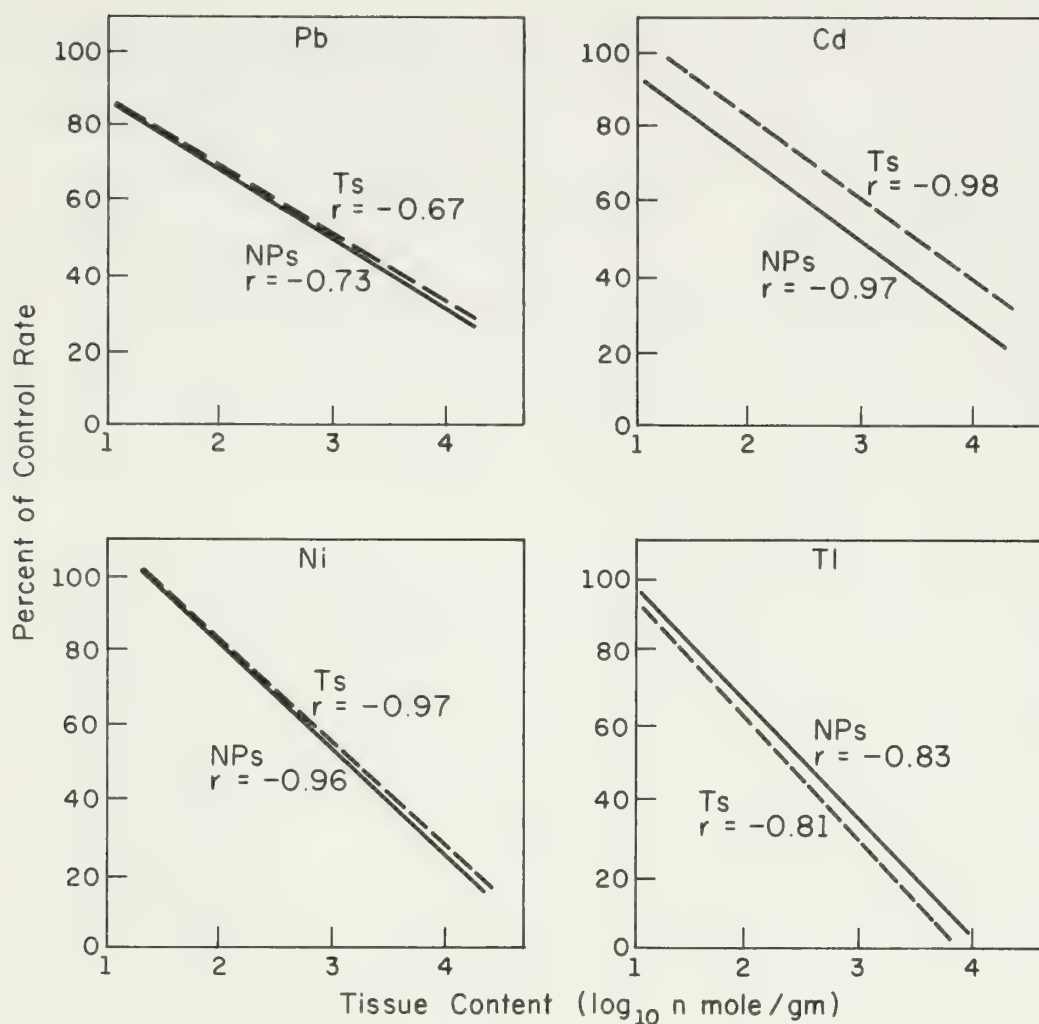


Figure 79. Relationship between Net Photosynthesis (NPS) and Transpiration (TS) at the End of the Time-Course Experiments with Excised Sunflower Tops Expressed in Terms of Leaf Tissue Content

with regards to the effect of Pb, Cd, Ni and Tl on photosynthesis and transpiration of whole plants. Heavy metal salts were added to the root solution of plants grown in hydroponic culture. Thus all the resistances to ion uptake and translocation were retained including root absorption and root and stem translocation as well as any defense mechanisms that plants might possess to avoid the toxicity of heavy metals.

Plants were germinated from seed and grown in hydroponic culture of full strength Hoagland solution in a glasshouse supplemented with artificial light. At 2-4 weeks of age these plants were transferred to fresh Hoagland solution and heavy metal added to give various concentrations (0.5-20 ppm Cd, Tl or Ni, or 1-500 ppm Pb). Rates of net photosynthesis and transpiration, total plant biomass and heavy metal content of leaf tissue were measured 4-7 days after treatment.

The rate of net photosynthesis was reduced more in Tl-treated plants of both sunflower and corn than for any of the other heavy metals tested (Figure 80). Photosynthesis of Cd-treated plants was reduced by a lesser amount to  $70 \pm 10$  percent of control plants. Ni was found to be slightly less toxic than Cd in both sunflower and corn

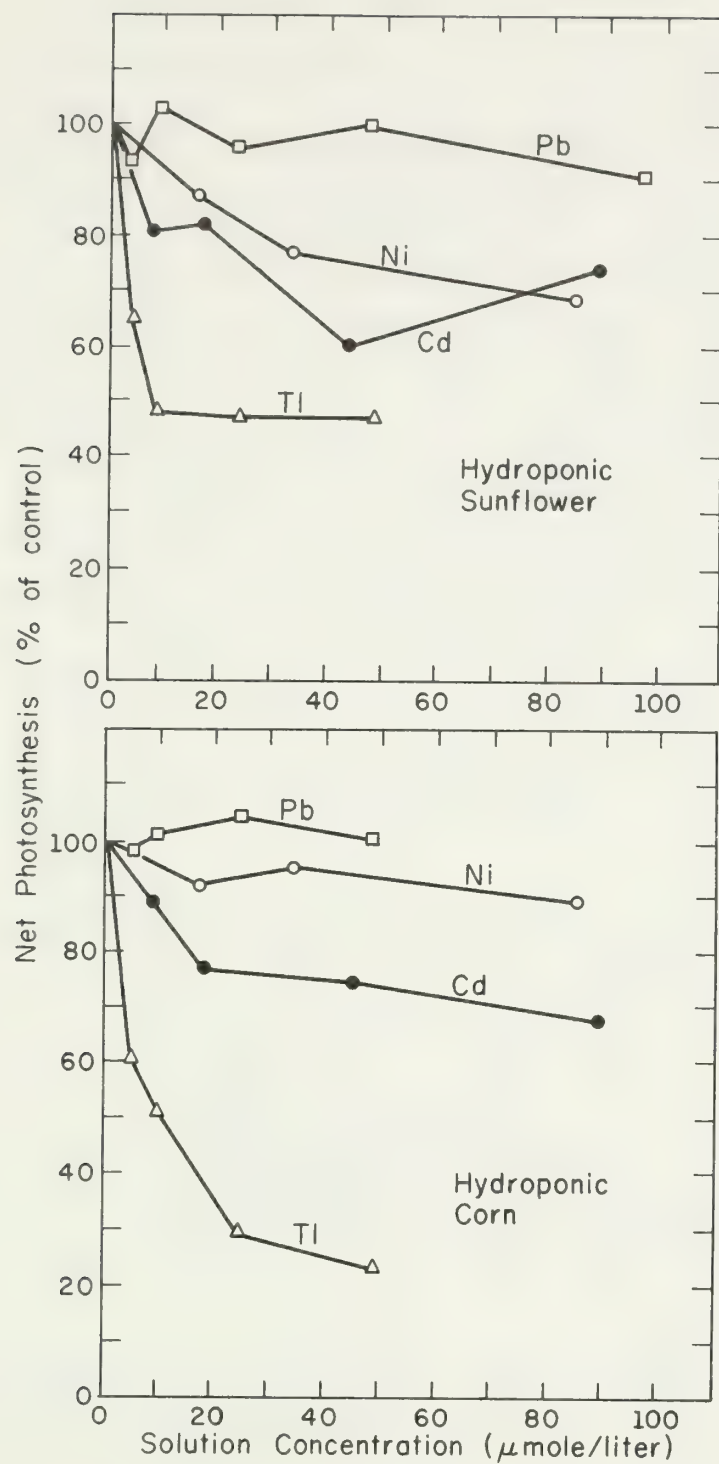


Figure 30. Relationship between Net Photosynthesis and Treatment Levels for Sunflower and Corn Grown in Hydroponic Culture

with photosynthetic rates of  $80 \pm 10$  and  $90 \pm 5$  percent, respectively. The rate of net photosynthesis of Pb-treated plants was not significantly different from that of control plants. This was true even when the treatment concentration was raised to 500 ppm.

The amount of Cd and Ni that accumulated in the leaves of sunflower was 2-3 times that found in corn (Figure 81). Tl accumulation was similar in both species to the relatively low amount observed for Ni in corn. The Pb content in leaves of both sunflower and corn treated with up to 500 ppm was not significantly different from that of control plants.

When rates of net photosynthesis are plotted against the heavy metal content of leaf tissues (Figure 82) the same general pattern is found for both species with Tl being most toxic followed by Cd and Ni. The regression slopes are more negative for corn indicating a greater sensitivity to heavy metal contamination for this species than that found for sunflower.

The rate of transpiration closely follows the decrease in photosynthetic rate for sunflower treated with Ni or Cd and for corn treated with Ni (Figure 83). This suggests that stomatal opening may be an important factor in the effect of certain heavy metals on plants. The photosynthetic

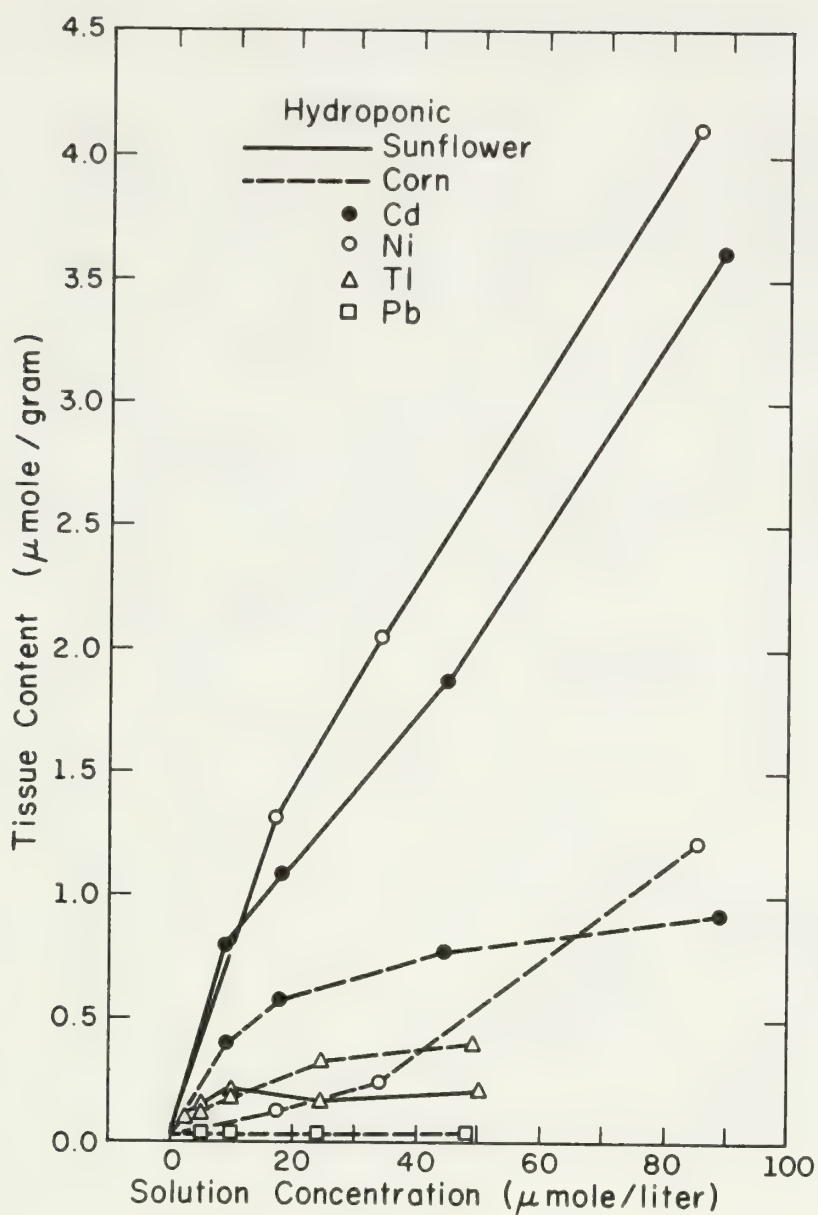


Figure 81

Accumulation of Heavy Metal Ions in Leaf Tissue of Sunflower and Corn Grown in Treatment Hydroponic Media

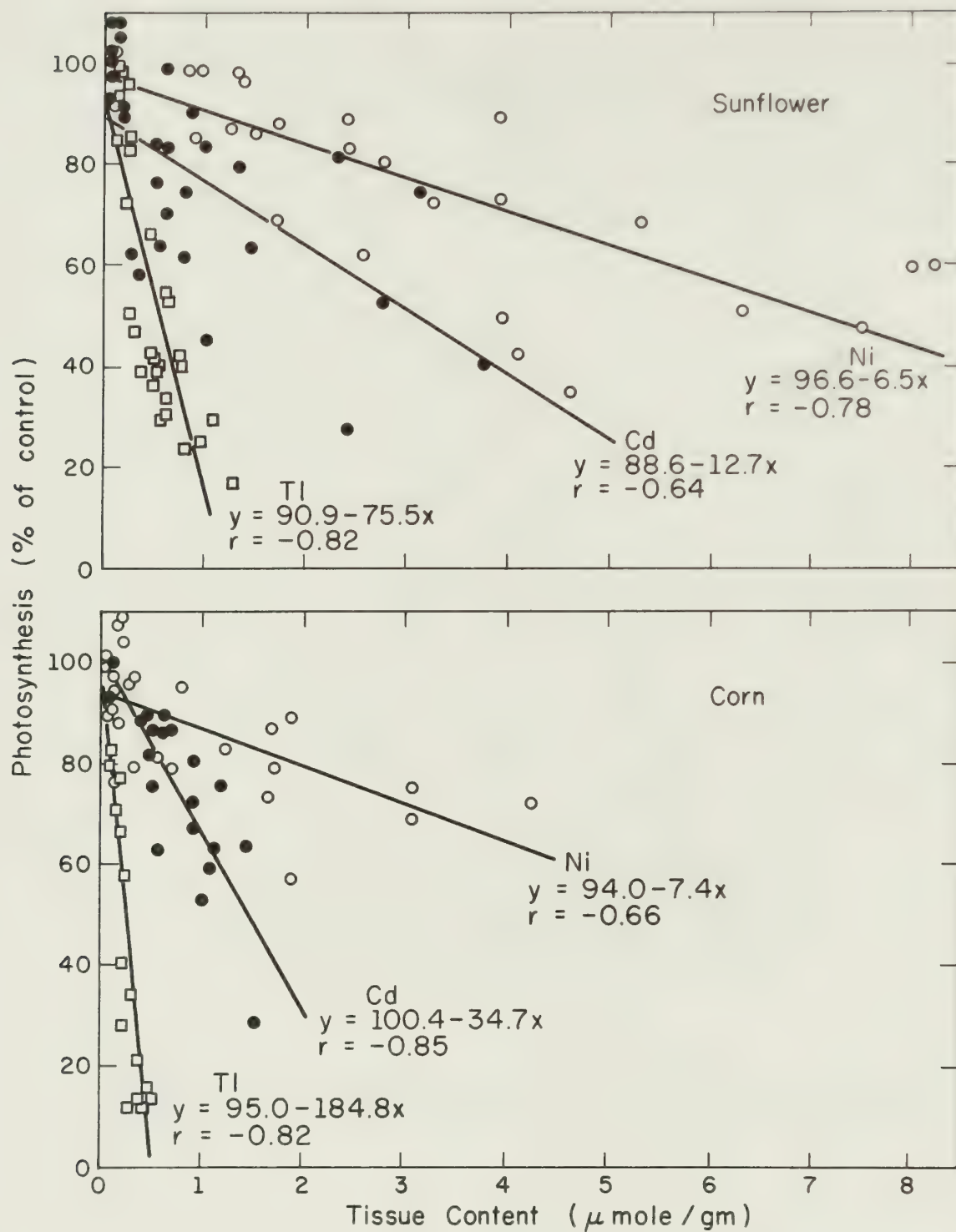


Figure 82

Relationship between Net Photosynthesis and Heavy Metal Content of Leaf Tissue of Sunflower and Corn Treated Hydroponically



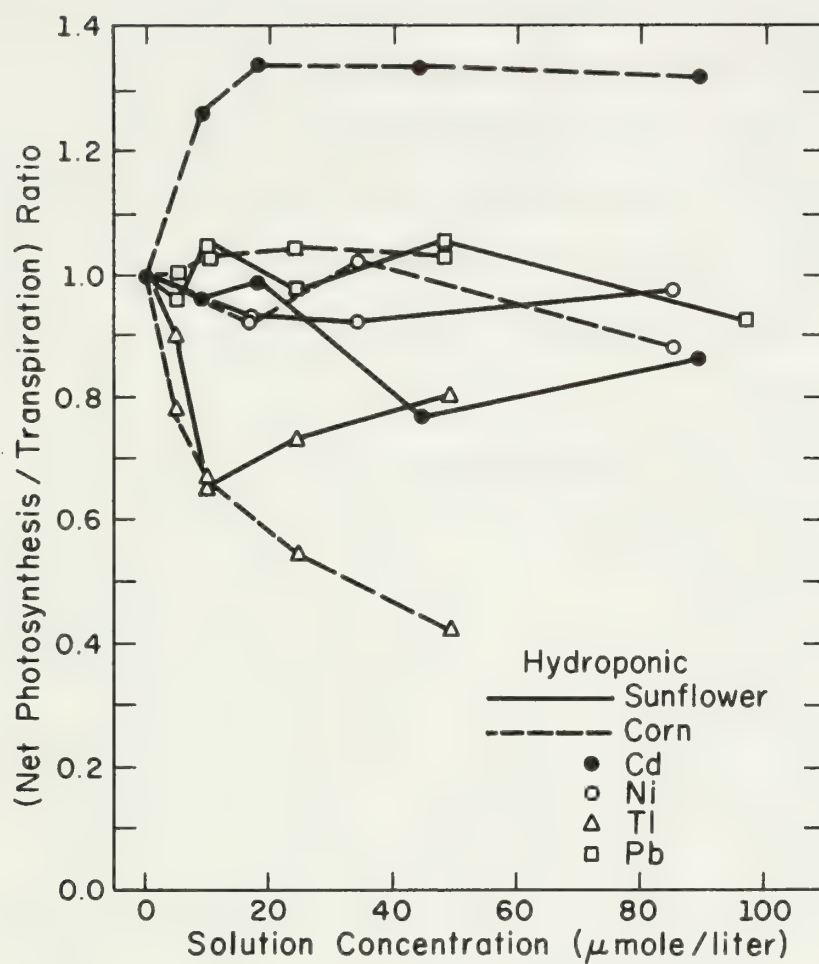


Figure 83

Relationship between Net Photosynthesis and Transpiration for Sunflower and Corn Treated with Various Heavy Metals in Hydroponic Culture

rate of Tl-treated plants was reduced more than the rate of transpiration indicating a direct effect of this heavy metal on biochemical and/or biophysical reactions associated with carbon dioxide uptake. In Cd-treated corn the rate of transpiration is lower than that of photosynthesis. This suggests that Cd is inhibiting root absorption and/or movement of water from the roots to the leaves in corn.

The results of experiments with excised sunflower tops and some of the data obtained from hydroponic studies indicate that heavy metal ions might be having a direct effect on stomatal opening. To test this hypothesis we conducted an experiment in which stomatal opening was measured directly as a function of heavy metal treatment. Abaxial epidermal peels were taken from leaves of untreated plants near the end of a nocturnal dark period, floated on deionized water and scored for stomatal opening. Peels with a low score, indicating the majority of the stomates to be closed, were incubated in the dark for 4 hrs in solutions of heavy metals, next exposed for 4 hrs to conditions which induce stomatal opening (high light intensity and reduced CO<sub>2</sub> concentration) and placed back in the dark for 4 hrs. Stomatal opening was measured at the end of each 4 hr period with the aid of a microscope.

The effect of heavy metals on the opening of closed stomata at various solution concentrations (Figure 84) closely resembles the log-linear relationship found for the effect of these same heavy metals on photosynthesis and transpiration of excised sunflower tops (Figure 79). This tends to confirm the hypothesis of heavy metals having a direct effect on stomatal opening. The similarity between the effect of Pb, Cd and Ni on stomata opening suggests that if Pb were present in the vicinity of the stomata of whole plants to the extent found for other heavy metals it too would cause reduction in photosynthesis. Our data indicate that Pb is not translocated from roots to leaves of plants grown in hydroponic media for short periods of time. However, plants grown in Pb-treated vermiculite (PR2, p. 241-243; PR3, p. 151-156; Bazzaz, Rolfe and Windle, 1974) or soil (Rolfe, 1973 and personal communication) do accumulate enough Pb over long time periods (30-60 days) to cause significant reductions in photosynthesis and transpiration. In these studies photosynthesis and transpiration declined concomitantly with increasing leaf Pb content suggesting that stomata may be an important controlling factor under these conditions also.

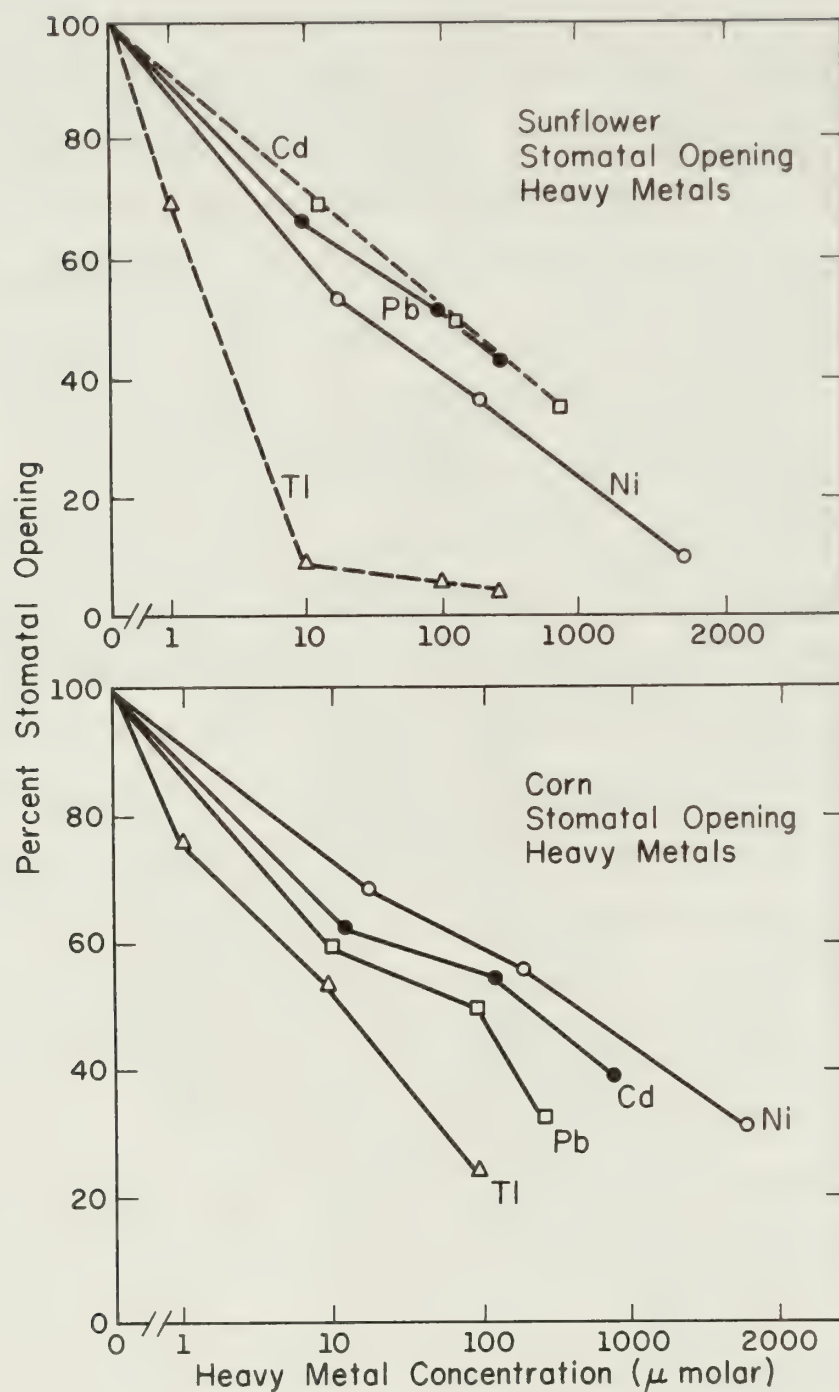


Figure 84

Effect of Various Heavy Metals on the Opening of Closed Stomata of Sunflower and Corn. Epidermal Peels Were Floated on Solutions of Heavy Metals and Stomatal Opening Measured with the Aid of a Microscope

## 2. Aerosol Studies

Lead may also enter plants via aerial deposition. This may be extremely important to plant growth since Pb entering the plant directly from the air must pass through stomata and thus the probability of coming in contact with the stomatal apparatus, and possibly causing stomatal closure, would be very large. Plants may also be viewed from the standpoint of removing aerosol particles from the bulk air and thus may function as a filter. We have completed some preliminary experiments designed to answer these questions.

The aerosol generator, wind tunnel and fumigation chamber proposed and described earlier (PR3, p. 167-173) have been completed and tested. All experiments described below were conducted at a windspeed of  $16.4 \text{ M min}^{-1}$  (6.1 mph), an aerosol flux of  $3 \text{ } \mu\text{g M}^{-3}$  ( $45.9 \text{ } \mu\text{g min}^{-1}$  for the  $1 \text{ ft}^2$  cross-sectional area of the fumigation chamber), and a particle size of approximately 5 micron in diameter. Each fumigation run lasted for approximately 30 min. Light intensity was maintained at approximately 2,000 ft-c, relative humidity at 55-60% and air temperature at  $24\text{-}28^\circ\text{C}$ . The wind tunnel and fumigation chamber was designed and constructed with induced flow and absolute particle filters to minimize contamination of the ambient



air. Even so it was decided to further reduce Pb contamination by attempting to do some of the preliminary experiments with particles of a material other than Pb. Therefore, an experiment was conducted to determine the similarity in gross deposition on plants between particles of Pb and those of a uranine dye which can be easily measured fluorometrically. Sunflower plants were pruned of all leaves within 20 cm of their tops except for 1 large leaf and several smaller ones. The plant top was positioned in the fumigation chamber so that the large leaf was horizontal and trailed downwind of the stem. Thus, when the wind flow was turned on, the plant top assumed a stable position in the air stream with very little movement during fumigation. The aerosol load collected by sunflower plants fumigated with uranine was essentially identical to that of plants fumigated with  $\text{PbCl}_2$  particles (Figure 85). This gave us confidence that fumigation with uranine could be successfully substituted for Pb in at least some of the aerosol deposition experiments.

Two additional aerosol experiments have been completed. The first is a comparison of scavenging efficiency between rough pubescent leaves (sunflower) and relatively smooth non-pubescent leaves (tulip poplar). Single leaves were



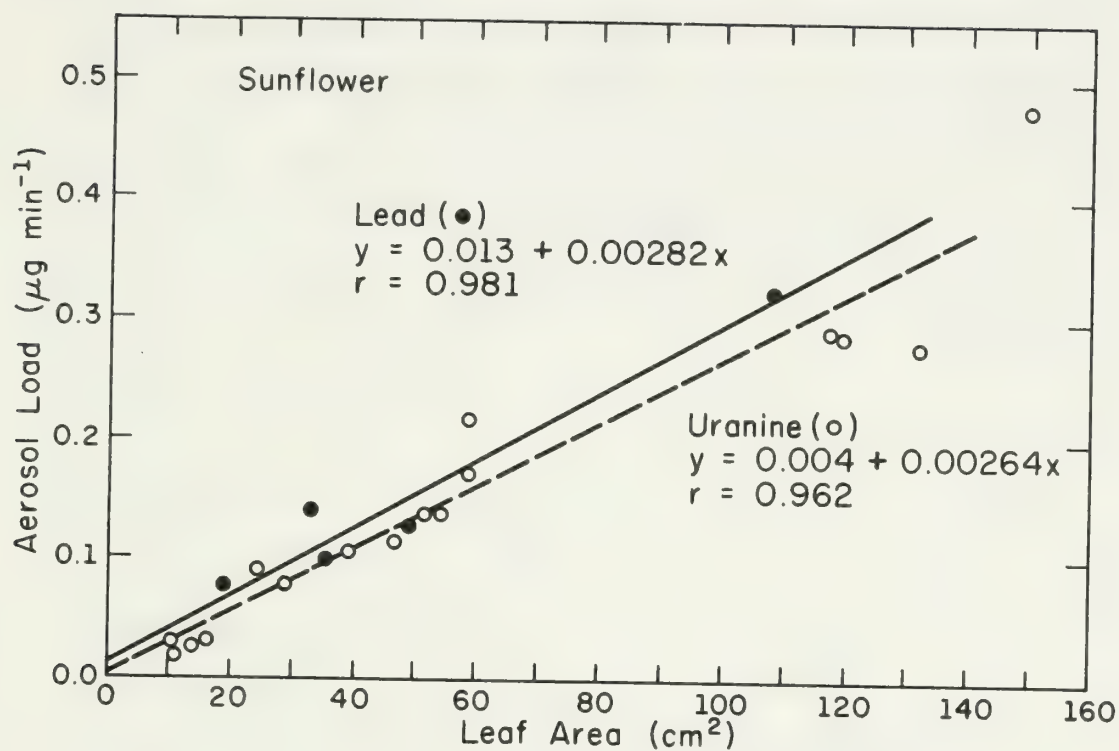


Figure 85

Correspondence in Aerosol Deposition (Approximately 5 Micron Diameter Particles) between  $\text{PbCl}_2$  and Uranine Dye Particles on Single Leaves of Sunflower.

positioned in the fumigation chamber as described above and fumigated with approximately 5 micron diameter uranine particles. The deposition rate for the pubescent leaves of sunflower is nearly 10 times that of the non-pubescent leaves of tulip poplar (Figure 86). Since all other conditions during the fumigation of these two species were the same, we conclude that the difference in aerosol deposition is due only to differences in leaf surface characteristics.

In another experiment we examined the difference in aerosol deposition between a single trailing leaf and a group of assemblage consisted of placing the petioles of leaves into a perforated hollow "stem" filled with water. In this manner leaf number and leaf area can be varied over a wide range and by rotating the "stem" during fumigation a reasonable approximation to a tree can be modelled with flapping leaves and wind striking all sides of the assemblage. This not unlike the situation that an isolated tree might experience over time in an urban environment.

We found the rate of deposition for leaf assemblages to be essentially identical to that of single trailing

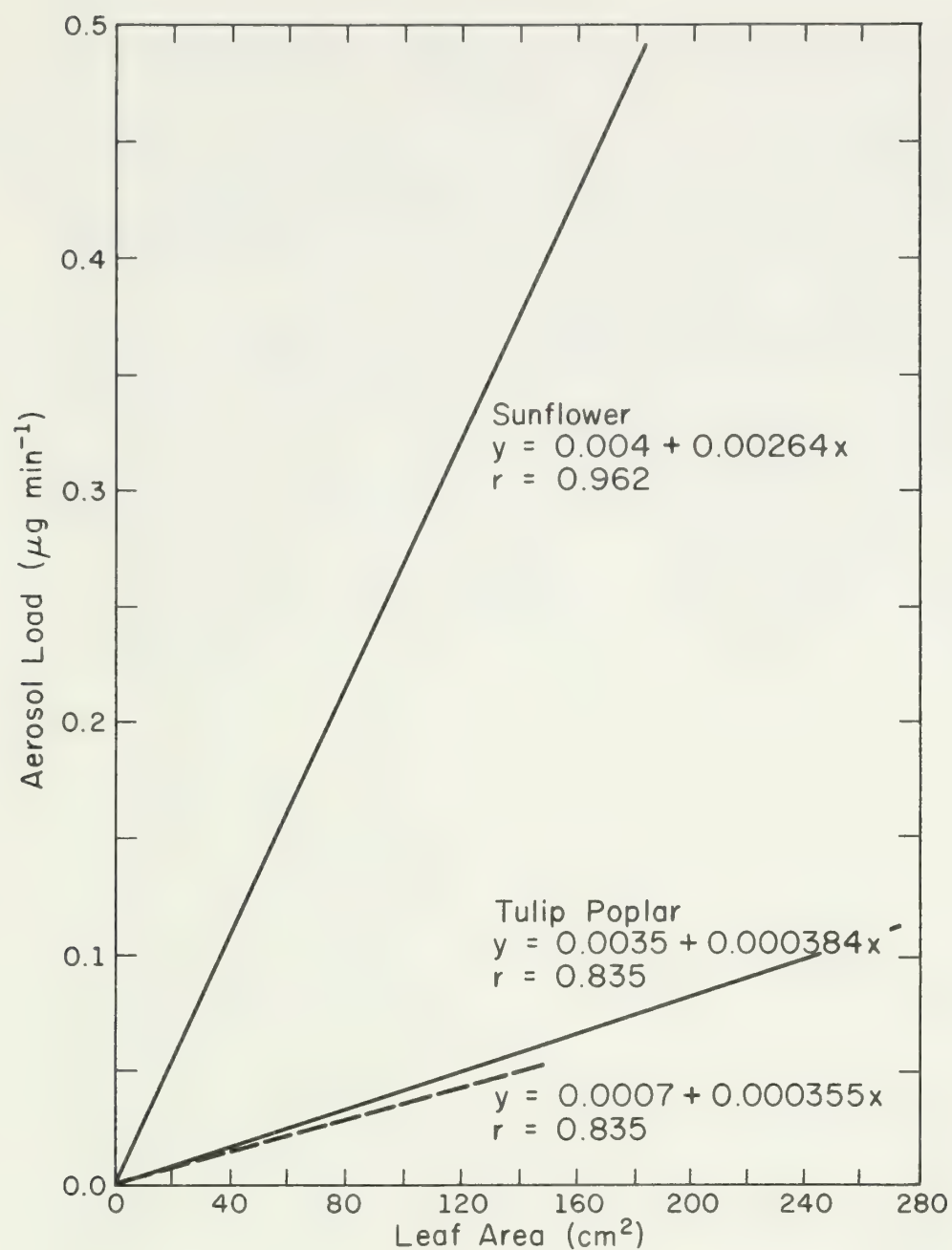


Figure 86

Deposition of Uranine Dye Particles (Approximately 5 Micron Diameter) on Single Leaves (Dashed Line) and Leaf Assemblages (Solid Line) of Tulip Poplar and Single Leaves of Sunflower

leaves (Figure 86). This suggests that experiments with single leaves may be a sufficient indicator of the scavenging efficiency of leaf assemblages and that the physical processes responsible for adsorption of particles may be the same for streamlining leaves as they are for leaves in extremely turbulent flow. However, the adsorption processes of leaf assemblages could be interacting in such a way as to give the appearance of results identical to that of single leaves and thus obscure any real differences between them. We are planning experiments to answer this question.

### References

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### 3. Lateral Root Effects

Attempts to localize cadmium accumulated by hydroponically grown corn have not been successful thus far; however, it was noted that small amounts of cadmium in solution decreased the number of lateral roots formed. It was then decided to conduct a series of experiments that would elucidate the effects of lead and cadmium on lateral roots in corn and soybeans. Plants (either corn or soybeans) were grown in complete Hoaglands solution for two weeks before treatment with heavy metals. At the time of treatment, 4 plants were transferred to a 12 liter tub of complete Hoaglands. After 24 hours, heavy metals were added to the hydroponic solutions.

Results from 10 separate experiments can be seen in Table 36. As little as  $100 \mu\text{g Cd}^{++}/\text{l}$  as  $\text{CdCl}_2$  significantly reduced the number of lateral roots formed in corn. (Figures 87-89) However, Cd had no effect on lateral root formation in soybean. It can also be seen from Table 37 that lead had no effect on lateral root formation in corn and soybean. Excessive lead (above  $2500 \mu\text{g Pb}^{++}/\text{l}$ ) had a general stunting effect. In another series of experiments, it was found that lower levels of Cd that would inhibit lateral root formation did not inhibit root elongation (Table 38).



Table 36

Cd<sup>++</sup> in µg/l of Hoaglands Solution

		0	100	250	500	1000
No. of laterals/ apical 10 cm	Corn	72	54*	38*	42*	36*
	Soybean	50	49	48	49	52

\*Indicates significance at the 1% level.

Table 37

Pb<sup>++</sup> in µg/l of Hoaglands Solution

		0	1000	5000	10000	25000
No. of laterals/ apical 10 cm	Corn	66	67	52	56	65
	Soybean	41	38	32	45	36

Table 38

Cd<sup>++</sup> in µg/l of Hoaglands Solution

	0	100	250	500	1000
mM of root growth in 3 days for corn	12	14	11	11	9

## Figures 87-89

Light Micrographs of Corn Roots Grown in Hydroponic Solution.

Figure 87 . Normal root showing lateral root initials

(arrows). Figure 88. Root treated with 2 ppm  $\text{Cd}^{++}$ .

Note decrease in number of laterals formed. Figure 89 .

Root treated with 20 ppm  $\text{Cd}^{++}$ . Note abnormal development

of roots near apex.

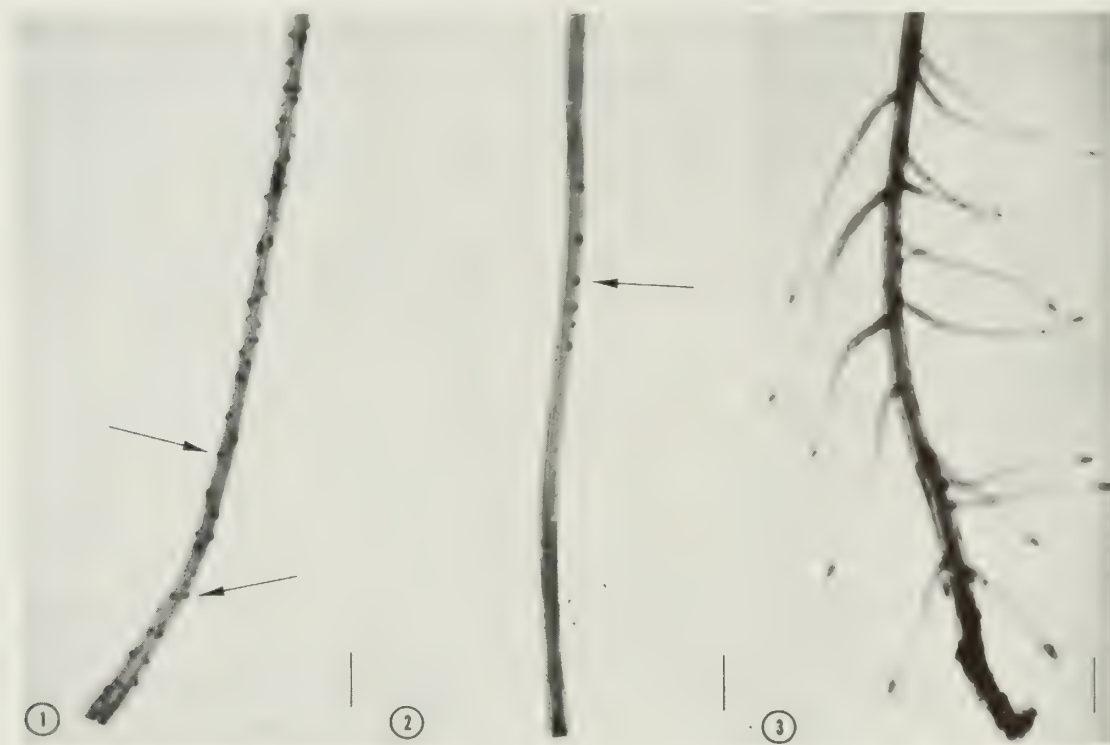


Figure 87

Figure 88

Figure 89

#### 4. Sorption of Heavy Metal Cations by Corn Mitochondria and the Effects on Electron and Energy Transfer Reactions

##### Background

Certain trace metals such as Pb and Cd that may occur in various parts of the agricultural environment have been reported to inhibit plant growth under some conditions (Haghiri, 1973; John et al., 1972; Miller and Koeppe, 1970; Page et al., 1972). Although the specific causes of the observed toxic effect of trace metals have not been pinpointed, the nonbeneficial effects reported for trace metals on electron and energy transfer reactions in plant mitochondria may be implicated (Koeppe and Miller, 1970; Miller and Koeppe, 1970; Miller and Bittell, et al., 1973; Miller and Dumford, et al., 1970). Lead at low concentrations (10-50  $\mu\text{M}$ ) has been reported to stimulate oxidation of exogenous reduced nicotinamide-adenine dinucleotide (NADH) and to inhibit succinate oxidation by isolated corn mitochondria (Koeppe and Miller, 1970). Cadmium stimulated at low concentrations (10-50  $\mu\text{M}$ ) and inhibited at higher concentrations (>100  $\mu\text{M}$ ) the oxidation of NADH by isolated corn mitochondria (Miller and Bittell, et al., 1973). Additionally, Cd (250  $\mu\text{M}$ ) completely inhibited the phosphorylation associated with succinate oxidation.

Effects of trace metals on mitochondrial membranes have also been reported (Miller and Bittell, et al., 1973). Lead and Cd induced swelling (as measured by percent transmittance changes) of isolated corn mitochondria has been observed. Whether the same cation site is responsible for both the oxidative-phosphorylative and membrane effects is not known. Moreover, little is known about the number of sites of metal action in plant mitochondria, or if these sites vary with different divalent metal ions. Mitochondria from animal sources have been reported to bind cations in the absence of metabolism (Chappell et al., 1963; Scarpa and Azzi, 1968; Slater and Cleland, 1953). Such passive divalent cation binding is most often discussed as it relates to the energy-linked ion translocation of common physiological cations such as  $\text{Ca}^{+2}$  (Scarpa and Azzi, 1968; and Scarpa and Azzone, 1968). This report details the passive binding characteristics of a series of divalent cations and the effects of the cations on the oxidative, phosphorylative, and membrane swelling characteristics of isolated corn mitochondria.

## 2. Materials and Methods

Corn seedlings (Zea mays L., Wf9 x M14) were grown on paper towelling saturated with 0.1 mM  $\text{CaCl}_2$  ( $29 \pm$

0.5°C). Mitochondria were isolated from three-day-old etiolated shoots by the procedure of Miller and Dumford et al., 1970.

Mitochondrial cation sorption experiments were performed at room temperature using the dye Murexide (ammonium purpurate) as a spectroscopic probe of cation concentration (Mela and Chance, 1968). The absorbance difference between 510 nm and 540 nm resulting from the spectral shift that occurred when the dye formed a weak complex with the metal cations was monitored using an Aminco dual wavelength UV/visible DW-2 spectrophotometer. Cation sorption was measured on 3 ml suspensions of mitochondria (approximately 1 mg of protein) in 0.3 M sucrose, 20 mM Tris-HCl (pH 7.5) and 40  $\mu$ M Murexide. The cation sorbed was taken as the difference between the initial cation added to the mitochondrial suspension and the amount measured in solution 8 min after the cation addition.

Respiratory, phosphorylation, and swelling-contraction experiments were performed with a mitochondrial suspension (approximately 1 mg of protein) in a filled 4 ml glass temperature-controlled ( $27 \pm 0.2^\circ\text{C}$ ) reaction cell. The reaction medium contained 200 mM KCl, 20 mM Tris-HCl (pH 7.5) and 1 mg/ml bovine serum albumin (BSA). Other additions as indicated were 16  $\mu$ mol  $\text{KH}_2\text{PO}_4$ , 2  $\mu$ mol NADH,



40  $\mu\text{mol}$  malate plus 50  $\mu\text{mol}$  pyruvate, or 300 nmol adenosine, diphosphate (ADP). The reaction cell was equipped with a Clark Oxygen electrode (Yellow Springs Instrument Co.) and positioned in the light path of a Bausch and Lomb spectronic 70 spectrophotometer. Cell contents were stirred with a magnetic stirrer. The polarographically measured oxygen content of the solution and the percent light transmittance at 520 nm were simultaneously recorded on a dual channel strip chart recorder. An increase in transmittance corresponded to swelling and a decrease to contraction. Mitochondrial protein was determined by the procedure of Lowry et al., 1951.

### 3. Results

Cation Sorption - The passive sorption of  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Mn}^{+2}$  by isolated corn mitochondria in buffered sucrose solution was determined for cation concentrations from 10 to 100  $\mu\text{M}$ . A double reciprocal plot of cation adsorbed versus the cation concentration resulted in straight lines (Figure 90). The intercept on the ordinate corresponds to the maximal binding capacity of the mitochondria for each cation (Scarpa and Azzi, 1968). Within experimental error the binding capacity is equal for all the cations studied except  $\text{Pb}^{+2}$ . The maximum



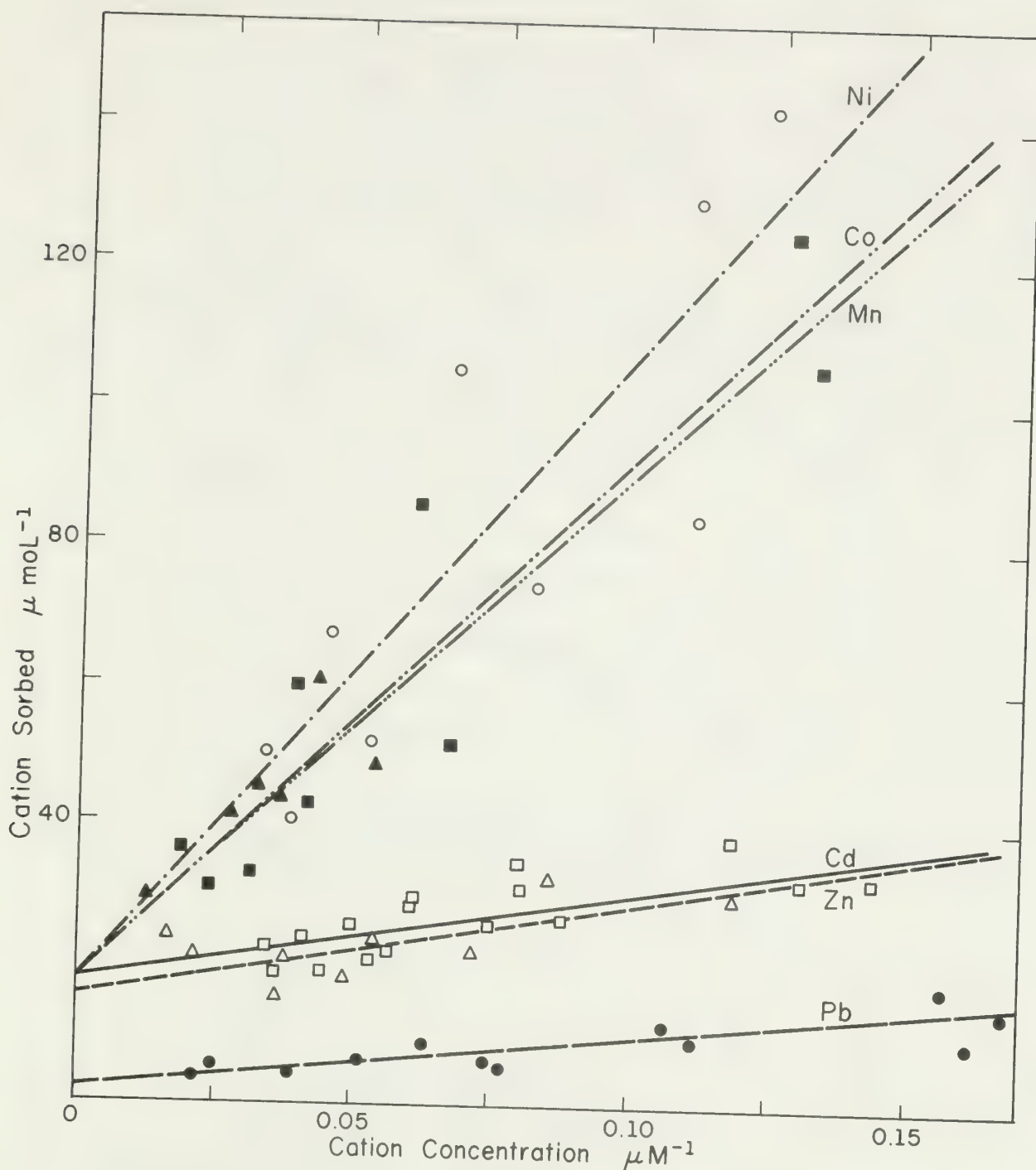


Figure 9C

Double Reciprocal Plot of Cation Sorption to Corn Mitochondria. Cation concentrations in the mitochondrial reaction media were measured using murexide (ammonium purpurate) as a spectroscopic probe. Further details of this technique are given in the Materials and Methods section. Linear regression lines calculated from data points are shown for each cation. ● Pb<sup>2+</sup>, □ Cd<sup>2+</sup>, △ Zn<sup>2+</sup>, ○ Ni<sup>2+</sup>, ■ Co<sup>2+</sup>, ▲ Mn<sup>2+</sup>.

binding of  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Mn}^{+2}$  was about 58 nmol per milligram of mitochondrial protein while the capacity for binding  $\text{Pb}^{+2}$  was apparently about ten times greater.

The intercept of the Plot on the abscissa is a measure of the affinity of the cation for its binding site (Scarpa and Azzi, 1968). The more negative the intercept, the higher the affinity of the cation for the binding sites and the more cation bound at lower solution concentration. The data suggest that the binding affinity of  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$  was considerably greater than that of  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Pb}^{+2}$ . While the binding affinity of  $\text{Pb}^{+2}$  was less than that of  $\text{Cd}^{+2}$  or  $\text{Zn}^{+2}$ , more  $\text{Pb}^{+2}$  was apparently bound than  $\text{Cd}^{+2}$  or  $\text{Zn}^{+2}$  even at the lower concentrations because of the ten-times greater number of  $\text{Pb}^{+2}$  binding sites.

Electron Transport - The effects of  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Ni}^{+2}$  on the rate of oxidation of succinate, exogenous NADH and malate + pyruvate are shown in Figure 91. The previously reported effects of  $\text{Cd}^{+2}$  on the oxidation rates for each substrate are included in Figure 91 for comparison (Miller and Bittell, et al., 1973). Of the three substrates, succinate was inhibited most severely at the lowest

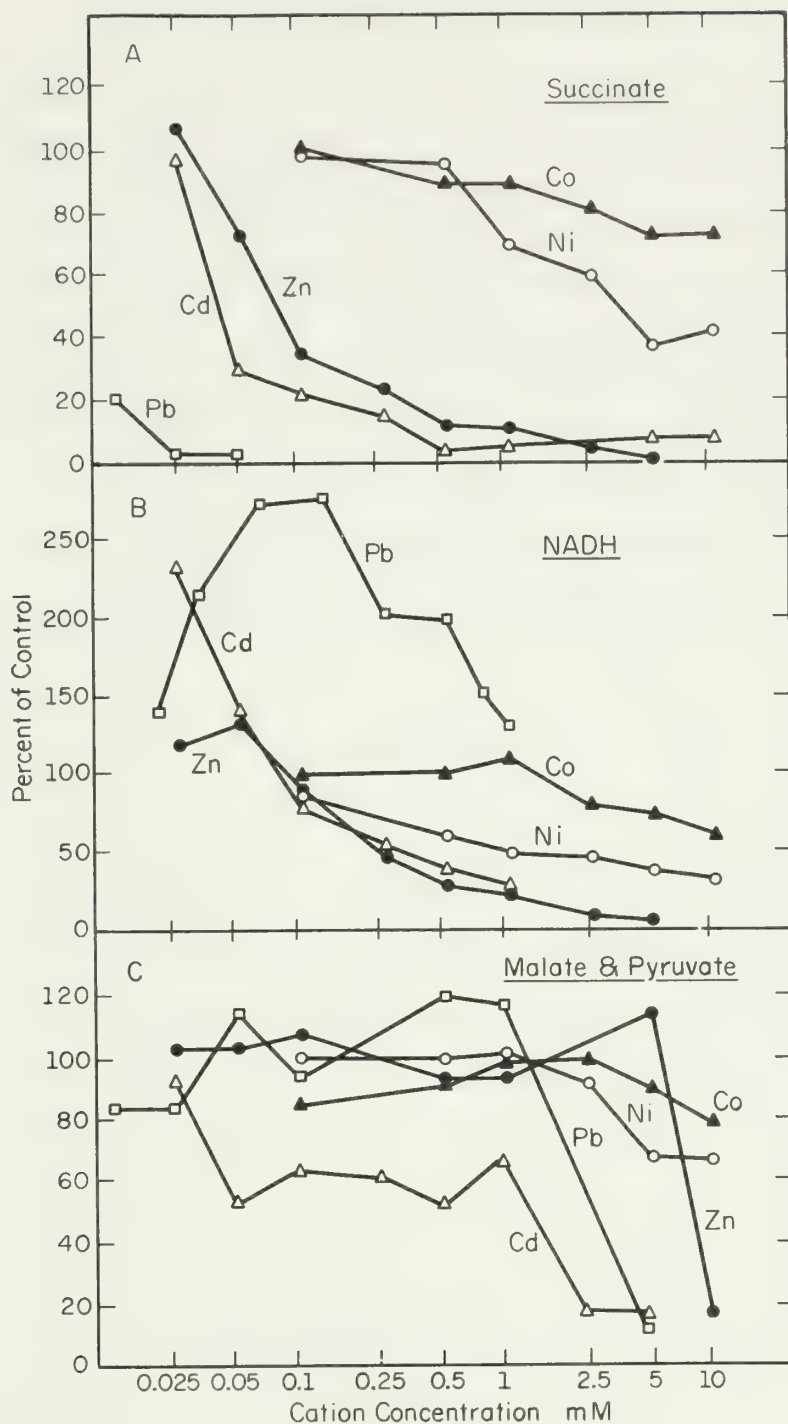


Figure 91

The Effect of Cation Concentration on the Acceptorless (Minus Phosphate) Substrate Oxidation of Corn Mitochondria. The reaction conditions were as given in the Materials and Methods section. Substrate was added 2.5 minutes after the addition of mitochondria to the medium, and cation was added 1.5 minutes later. Data are presented as the % of control with the control being the rate of  $O_2$  uptake before cation addition and the experimental that rate after cation addition. Substrates were succinate (A), NADH (B), and malate + pyruvate (C). Symbols as in Figure 90.

concentrations ( $\sim 50 \mu\text{M}$ ) by  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ , and  $\text{Zn}^{+2}$ , while  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  had little effect until concentrations of 1 mM or greater were reached. Effects of  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ , and  $\text{Cd}^{+2}$  on exogenous NADH oxidation include stimulation at low concentrations and inhibition at higher concentrations. With all cations the effects on oxidation observed during malate + pyruvate respiration were considerably less pronounced than during either exogenous NADH or succinate respiration.

Phosphorylation - The effects of  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Ni}^{+2}$  on the ADP/O ratios during succinate, exogenous NADH, and malate + pyruvate oxidation are compared in Figure 92. Both succinate and exogenous NADH phosphorylation were uncoupled at similar concentrations for a given cation. Phosphorylation was uncoupled by  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$  at 0.5 to 1.0 mM while 10 mM or above  $\text{Co}^{+2}$  or  $\text{Ni}^{+2}$  was required for complete uncoupling. During malate + pyruvate oxidation, phosphorylation was not eliminated until the  $\text{Zn}^{+2}$  or  $\text{Cd}^{+2}$  concentration was 5 mM.

The effect of  $\text{Pb}^{+2}$  on phosphorylation is not reported since addition of  $\text{Pb}^{+2}$  to mitochondrial suspensions containing the phosphate necessary for phosphorylation resulted in formation of a precipitate assumed to be a lead phosphate.

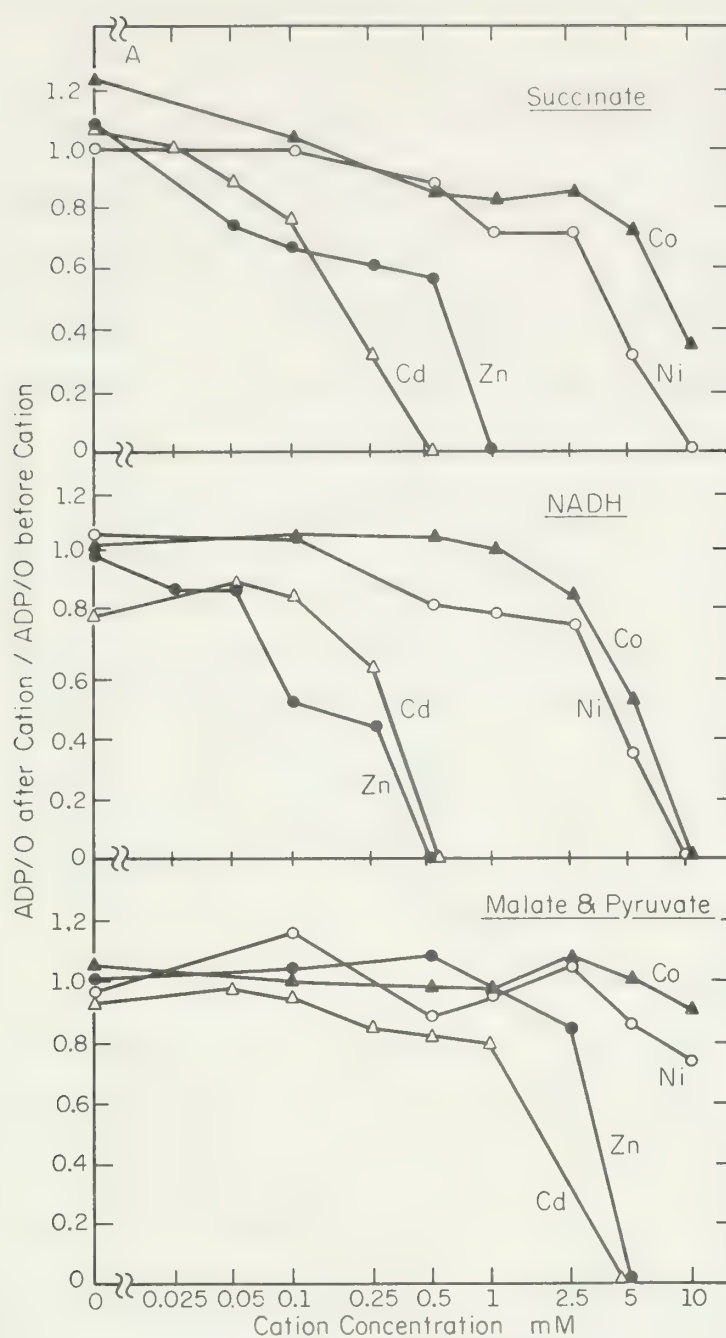


Figure 92

The Effects of Cation Concentration on the ADP/O Ratio of Corn Mitochondria during Substrate Oxidation. The reaction conditions were as given in the Materials and Methods section and contained 4 mM  $\text{KH}_2\text{PO}_4$ . Substrate was added 1 minute after addition of mitochondria to the reaction medium and ADP was added 1.5 minutes later. After return to state 4, the cation was added, followed by a second addition of ADP. Substrates used were succinate (A), NADH (B) and malate + pyruvate (C). Symbols as in Figure 90.



Swelling and Contraction - The % transmittance changes induced in corn mitochondria during succinate oxidation by 0.1 mM solutions of  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Ni}^{+2}$  are shown in Figure 93. Such increases in light transmission have been shown to correspond to an increase in volume or swelling of the mitochondria (Lorimer and Miller, 1969). Neither  $\text{Ni}^{+2}$  nor  $\text{Co}^{+2}$  had any effect on the % transmittance of mitochondria under the above conditions, while  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ , and  $\text{Cd}^{+2}$  caused a decrease in the % transmittance to varying degrees. Although not shown, results during NADH oxidation were similar. During malate + pyruvate oxidation few changes in absorbance were observed.

#### 4. Discussion

Several studies with isolated mitochondria indicate that cations may be bound in the absence of metabolism (Chappell et al., 1963; Scarpa and Azzi, 1968; Scarpa and Azzone, 1968; Scarpa, 1969; Slater and Cleland, 1953; and Azzi, 1968) report that the maximum binding capacity of  $\text{Ca}^{+2}$  and  $\text{Rb}^{+}$  is 25 and 50 nmol per milligram protein respectively to sonicated particles of rat liver mitochondria. From these results and similar data on the competition between ions for binding sites, they conclude that  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Rb}^{+}$  and  $\text{K}^{+}$  all have the same binding



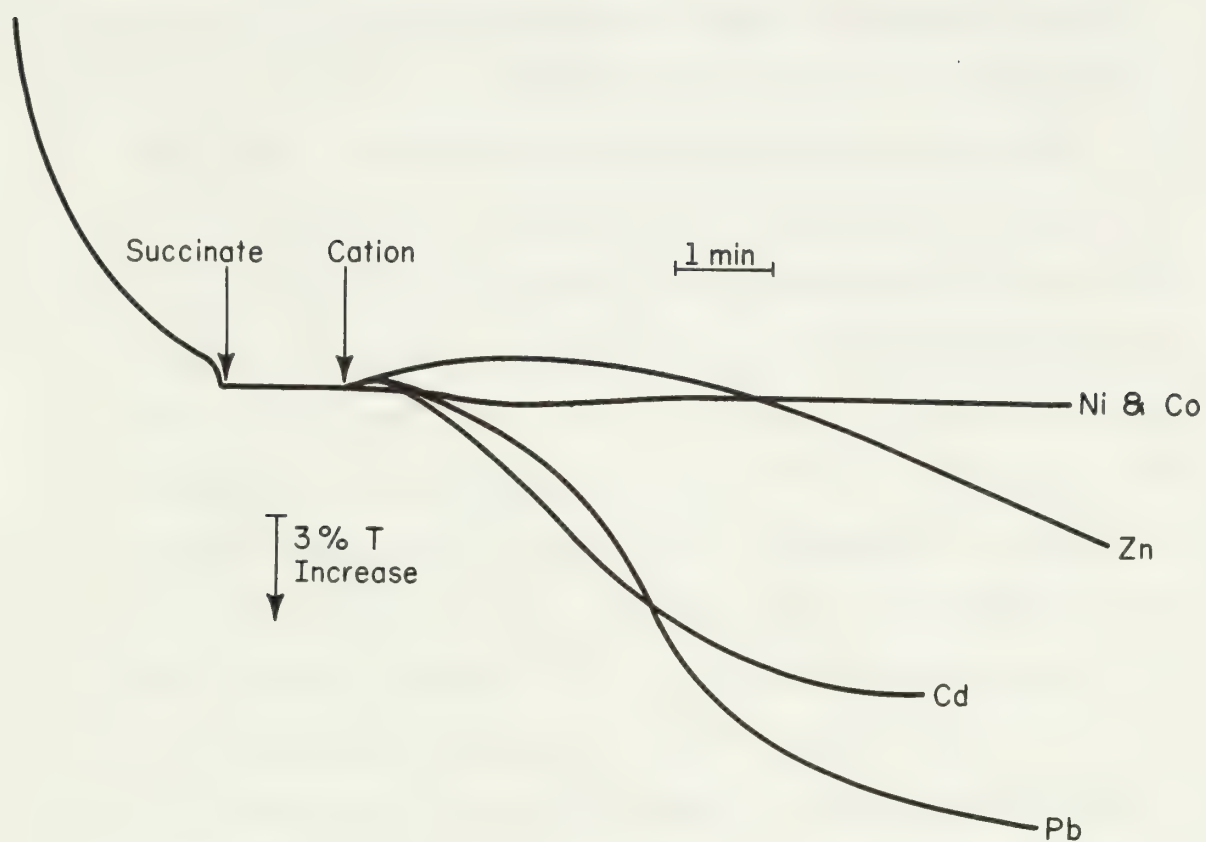


Figure 93

The Effect of 0.1 mM Cation on the Swelling (% Transmittance) of Corn Mitochondria during Succinate Respiration. The reaction conditions were as given in the Materials and Methods section.

site in mitochondria. The approximately two times greater binding capacity (58 nmol divalent cation per milligram of protein) indicated for  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Mn}^{+2}$  to isolated corn mitochondria may reflect the differences between plant and animal mitochondria or may simply result from differences in experimental conditions. The equal binding capacity for the five cations mentioned does suggest that the binding sites are the same for each cation as proposed for animal mitochondria. Both phospholipids and proteins have been suggested as specific sites for cation binding. It has been shown that lipid depleted rat liver mitochondria bind less  $\text{Ca}^{+2}$  than nondepleted mitochondrial particles and that an addition of phospholipids increases the amount of  $\text{Ca}^{+2}$  bound (Scarpa, 1969). Efforts in this laboratory to measure the cation binding to lipid depleted corn mitochondria and the extracted lipid were inconclusive in that substantial binding to both fractions was observed. The sulfhydryl groups of protein have also been mentioned as a possible binding site since dithiothreitol, a sulfhydryl protecting agent, was reported to prevent some of the effects of  $\text{Cd}^{+2}$  on isolated corn mitochondria (Miller and Bittell et al., 1973).

The reason for the anomalously large sorption capacity observed for  $\text{Pb}^{+2}$  in isolated corn mitochondria is not fully understood. The large amount of  $\text{Pb}^{+2}$  removed from solution makes it unlikely that  $\text{Pb}^{+2}$  was simply binding to various sites in the mitochondria. More likely the  $\text{Pb}^{+2}$  was being removed from the solution by precipitation as some insoluble lead salt. Electron micrographs of lead-treated mitochondria show numerous electron dense areas in the mitochondria that would be consistent with small lead salt precipitates.

The sorption data indicate that  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$  were more strongly adsorbed than  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ , and  $\text{Mn}^{+2}$ . Such an affinity difference does correlate with the differences in the effect of the cations on electron transport and phosphorylation (ADP/O ratios). Both  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$  inhibited succinate and exogenous NADH oxidation more severely and at lower concentrations than  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  (Figure 91). Phosphorylation was uncoupled during succinate and exogenous NADH respiration by  $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$  at similar concentrations while significantly higher concentrations of  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  were required for the same effect (Figure 92). Higher concentrations of all cations were required to inhibit substrate oxidation or uncouple phosphorylation

during malate + pyruvate respiration. This substrate difference is probably due to the ability of malate + pyruvate to bind cations in competition with the mitochondria and reduce the free cation concentration in solution.

When correlating cation effects on the electron transport chain and the amount of passive sorption of cations, it should be noted that the reaction medium is an important consideration. A sucrose medium was chosen for the cation sorption measurements because it minimized optical density changes of the mitochondria and ionic competition for binding sites. Other reaction media used to measure the cation effects on the electron transport chain of mitochondria may necessitate somewhat higher cation concentrations to achieve similar sorption. For example, bovine serum albumin was reported to bind approximately 2.0-2.5  $\mu\text{g}/\text{mg}$   $\text{Cd}^{+2}$  when in a reaction medium with 0.2 M KCl and 20 mM Tris-HCl (pH 7.5) (Miller and Bittell et al., 1973). However, the differences in bonding affinity of the cations studied do seem to be reflected by the effects of the cations on electron transport even in the different reaction media.

The flavoproteins have been suggested as the site of  $\text{Cd}^{+2}$  action on isolated corn mitochondria (Miller and Bittell

et al., 1973). Since  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Ni}^{+2}$  all have the same number of binding sites and their inhibiting effects are similar during both succinate and exogenous NADH oxidation, the site of action may be on the portion of the electron transport chain common to both substrates. It has been suggested that the divalent cation stimulation of exogenous NADH oxidation (Figure 9) that is not observed during succinate oxidation indicates a unique cation site for NADH oxidation (Miller and Bittell et al., 1973). Alternatively, the cations could stimulate the rate of exogenous NADH oxidation by facilitating the movement of NADH to the enzyme without stimulating succinate oxidation if the movement of succinate to enzyme is not rate limiting. The mitochondrial swelling induced by certain cations offers evidence for a nonspecific increase in mitochondrial membrane permeability due to the cations. The degree of swelling caused by specific cations also roughly correlates with the extent of stimulation observed. Lead and  $\text{Cd}^{+2}$  caused the most pronounced swelling and the greatest stimulation while  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  caused little swelling or stimulation. Southern corn leaf blight (race T) toxin has also been reported to cause pronounced swelling of certain isolated corn mitochondria that is associated



with large stimulations of exogenous NADH oxidation (Gengenbach et al., 1973; Miller, 1971). Disruption of mitochondrial membranes by sonication also stimulates exogenous NADH oxidation.

Although the specific site of cation action cannot be specified at this time, the data do suggest that the site of action may be common to several cations. The affinities of various cations vary for the mitochondrial sites and are reflected in the effective concentrations of each cation. Moreover, other cation binding agents present in the reaction medium may be expected to compete for the cations with the mitochondrial sites and mediate the effective cation concentrations.



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## 5. Effects of Lead Chloride on Isolated Chloroplast Reactions

A report on this study was given in the previous Progress Report (PR3) pages 137-151. During the early portion of the present report period some of the experiments were repeated and the results of this study were reported in ENVIRONMENTAL LETTERS, 6(3), 175-191 (1974).

## 6. Effects of Cadmium Nitrate on Spectral Characteristics and Light Reactions of Isolated Chloroplasts

### Background

The release of Cd from smelters, combustion of fuels, degradation of tires, phosphate fertilizers, and pesticides makes it a major environmental contaminant. Human uptake, absorption, retention and subsequent toxicity by Cd from air, water and food are known (Friberg et al., 1971). The Cd aerosol settles down with dust and precipitation (see Kitamura, cited in Friberg et al., 1971), contaminating soils and plants; it accumulates in plants and soils near highways (Lagerweff and Specht, 1970) and smelters (Buchauer, 1973) and is taken up by plants grown in Cd rich soils (Lagerwerff, 1971; Schroeder and Balassa, 1963; Yamagata and Shigematsu, 1970). Cadmium has been shown to inhibit growth in several species of higher plants (Page et al., 1972) and *Chlorella* (Vallee and Ulmer, 1972). Plants grown in hypotonic media accumulate Cd in their roots and leaves (Haghiri, 1973); detached plant leaves immersed in 2 ppm Cd salts show a reduced rate of gas exchange in light as measured with an infra red gas analyzer (F. Bazzas, 1973, submitted for publication), probably attributable to increased

stomatal resistance. In order to clearly answer the question whether photosynthesis per se is inhibited by Cd, and if so, what are the site(s) of its action, we studied the effect of  $\text{Cd}(\text{NO}_3)_2$  on photosynthetic reactions in isolated chloroplasts from maize.

Our results show that indeed  $\text{Cd}^{2+}$  is a potent inhibitor of photosynthesis in chloroplasts; 0.5 mM  $\text{Cd}(\text{NO}_3)_2$  caused a complete inhibition of pigment system (PS)II reactions, in addition to changes in concentration and composition of pigments.

## 2. Materials and Methods

Mesophyll chloroplasts were isolated from maize leaves as described previously (Bazzaz and Govindjee, 1973). However, 0.05 M HEPES buffer (pH, 7.6) was substituted for Tris-HCl buffer in the isolation medium, and 0.1% BSA was added to the homogenizing but not to the suspension medium. The concentration of chlorophylls was determined according to Arnon, 1949.

The reduction of DCPIP was measured spectrophotometrically as described by Stemler and Govindjee, 1973. The effect of  $\text{KNO}_3$  or  $\text{Ca}(\text{NO}_3)_2$  on DCPIP photoreduction was tested to check whether the effect of cadmium was

specific or simply due to osmotic effect of salts on chloroplasts. Other details are given in the legend of Figure 94.

Absorption spectra were measured with a Bausch and Lomb spectronic 505 spectrophotometer equipped with an integrating sphere. Chlorophyll emission spectra were measured with a spectrofluorometer described in Shimony et al., 1967, the time course of Chl a fluorescence as in Munday and Govindjee, 1969) and the excitation spectra of Chl a fluorescence as in Yang and Govindjee, 1966). The excitation spectra were corrected for the spectral variation of the monochromator; other details are given in the legend of Figure 97.

Light induced absorbance change for the reaction center of pigment system I (P700) was measured by a split-beam difference spectrophotometer (Sybesma and Fowler, 1968). The 703 nm measuring beam, obtained through a monochromator, had a band width of 9.0 nm. The photomultiplier (Amperex 56 CVP) was protected by a 703 nm interference filter (band width, 12.5 nm). Samples were illuminated with 729 nm (band width, 9.0 nm) light (incident intensity,  $2 \times 10^4$  ergs  $\text{cm}^{-2}$   $\text{sec}^{-1}$ ).



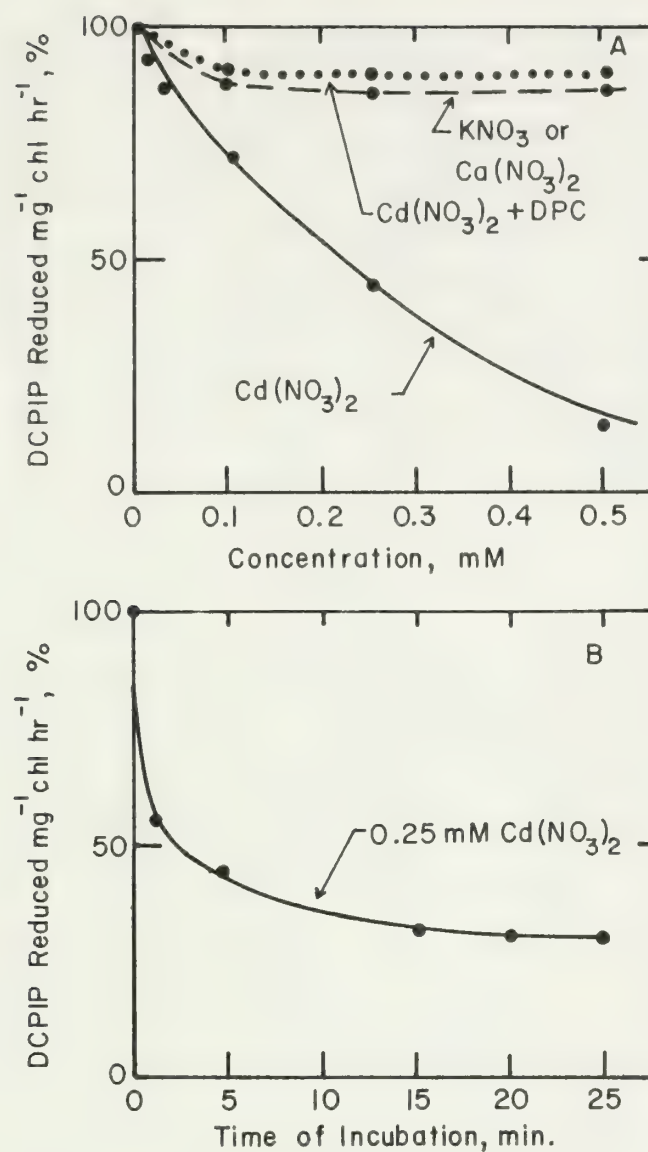


Figure 94

(A): Effects of  $\text{Cd}(\text{NO}_3)_2$  (\_\_\_\_),  $\text{KNO}_3$  or  $\text{Ca}(\text{NO}_3)_2$  (-----) and  $\text{Cd}(\text{NO}_3)_2 + \text{DPC}$  (.....) on saturated rates of DCPIP photoreduction in maize chloroplasts. Reaction mixture contained: 0.05M HEPES buffer (pH 7.6),  $5 \times 10^{-5}$  M DCPIP, 0.01M NaCl and 2.5  $\mu\text{g}$  chl. Chloroplasts were incubated for ten minutes in dark before measurements; other details in the text. 100% of control corresponds to 54  $\mu\text{moles DCPIP reduced mg}^{-1} \text{chl hr}^{-1}$ . Each point represents the average of five measurements. (B): Effects of 0.25mM  $\text{Cd}(\text{NO}_3)_2$  on the rates of DCPIP photoreduction in chloroplasts at different incubation periods.

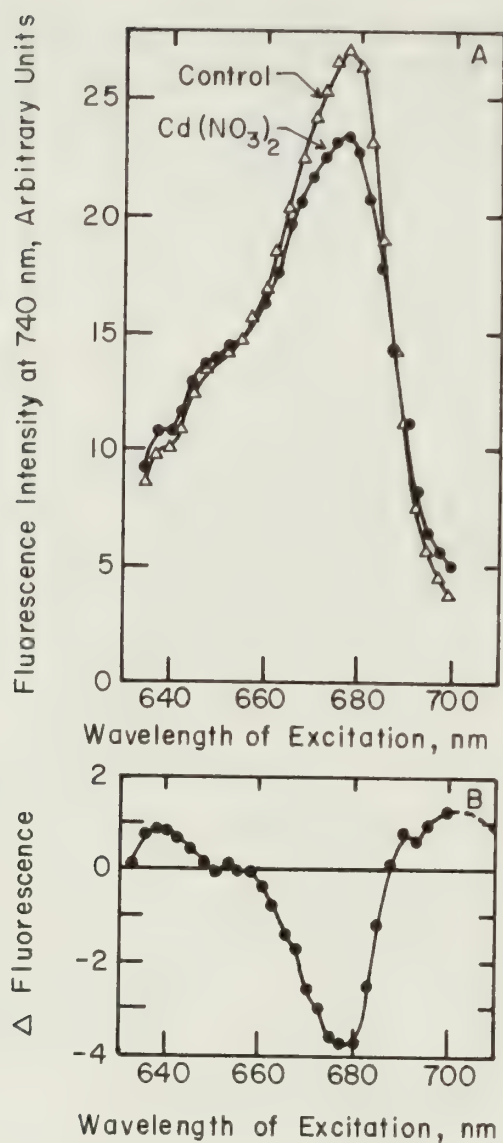


Figure 97

(A): Room temperature fluorescence excitation spectra of F740 of untreated (-Δ-) and treated (0.5mM  $\text{Cd}(\text{NO}_3)_2$ , -o-) chloroplast suspensions containing  $26 \mu\text{g Chl ml}^{-1}$  suspended in 0.05 HEPES buffer (pH, 7.6). The exciting slit had a half band width of 3.3 nm and the measuring slit of 16.5 nm.

(B): Difference fluorescence excitation spectrum of untreated (-Δ-) minus Cd treated (0.5mM, -o-) chloroplast suspensions.

### 3. Results and Discussion

#### (a) Inhibition of System II before Diphenyl-carbazide Donation Site

##### (1) Dichlorophenol Indophenol Photoreduction

Figure 94A shows the effects of different concentrations of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ , and  $\text{Ca}(\text{NO}_3)_2$  on DCPIP photoreduction in maize chloroplasts. 0.5 mM  $\text{Cd}(\text{NO}_3)_2$  inhibited this activity by 85%, whereas the other two salts, at the same concentration, decreased the same activity by only 10%. A short incubation period of chloroplasts with  $\text{Cd}(\text{NO}_3)_2$  was necessary to obtain maximum inhibition (Figure 94B); at 0.25 mM  $\text{Cd}(\text{NO}_3)_2$ , 50% inhibition was observed after one minute, and a 70% (maximum) inhibition was attained after 15 minutes of incubation.

The rate of DCPIP photoreduction in untreated chloroplasts was  $55 \mu\text{moles mg}^{-1} \text{ Chl hr}^{-1}$ . When chloroplasts were incubated for 10 minutes with 0.6 mM  $\text{Cd}(\text{NO}_3)_2$ , this rate was reduced to  $7 \mu\text{moles mg}^{-1} \text{ Chl hr}^{-1}$ . However, when both  $\text{Cd}(\text{NO}_3)_2$  and 0.15 mM DPC were added together, the rate was  $50 \mu\text{moles mg}^{-1} \text{ Chl hr}^{-1}$  showing the absence of inhibition by  $\text{Cd}(\text{NO}_3)_2$  for electron flow from DPC to DCPIP.  $10 \mu\text{M}$  3-(3,4 dichlorophenyl)-1,1 dimethyl urea (DCMU) caused complete inhibition of this reaction. The above results were confirmed in five experiments. We

conclude that the inhibition of PSII activity by  $\text{Cd}(\text{NO}_3)_2$  treatment is due to the inhibition of a reaction before the site of electron donation by DPC. [The latter is known to feed electrons to chloroplasts whose oxygen evolving ability is impaired by tris washing (0.8 M, pH 8.0) (Vernon and Shaw, 1969), the donation site being close to the first secondary electron donor (Y) of PSII, the primary electron donor being defined as the reaction center chlorophyll of PSII, see Butler, 1972.]

## (2) Chlorophyll a Fluorescence Induction

When dark adapted chloroplasts are illuminated with strong blue light, the chlorophyll a fluorescence level rises instantly to  $F_0$  (which reflects fluorescence intensity emitted from bulk pigments of PSII and PSI); thereafter it rises biphasically to a final level  $F_\infty$ . The fluorescence rise from  $F_0$  to  $F_\infty$  reflects the reduction of the "primary" electron acceptor of PSII (Q) to QH under conditions when the primary electron donor (Chl  $a_{\text{II}}$ , P680) is restored to its reduced state (Butler, 1972). If cadmium causes inhibition of PSII at the water oxidation level, the reduction of Q to QH would be impaired due to lack of electron (hydrogen) supply, and a reduced level of variable to constant fluorescence would be expected. Indeed, this was observed (Figure 95); the variable fluorescence ( $F_\infty - F_0$ )

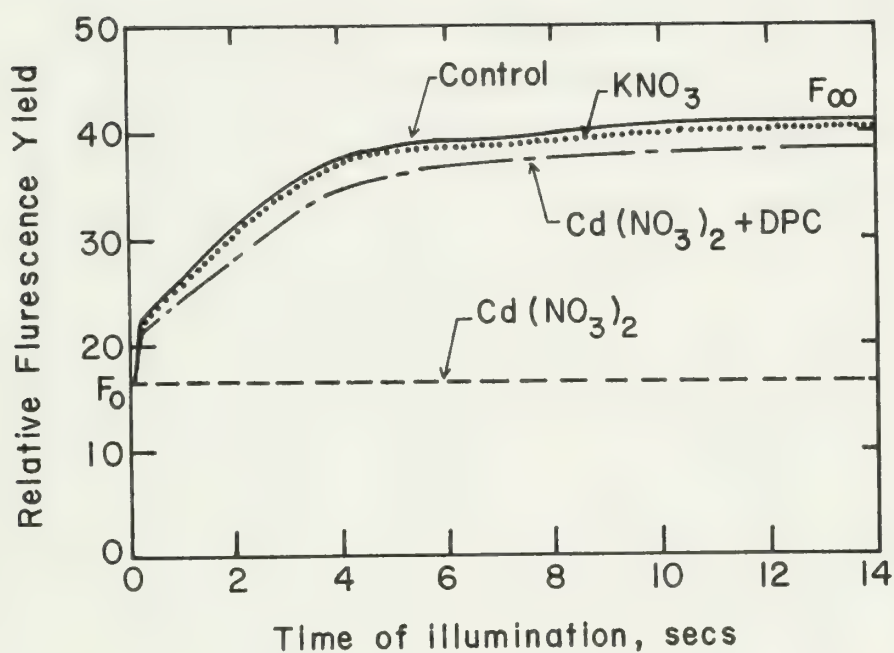


Figure 95

Effects of 0.5mM  $\text{Cd}(\text{NO}_3)_2$  (---), 0.5mM  $\text{KNO}_3$  (...) and 0.5mM  $\text{Cd}(\text{NO}_3)_2$  plus 0.5mM DPC (— - —) on the time course of Chl a fluorescence yield at 685 nm. Chloroplasts containing  $15 \mu\text{g Chl ml}^{-1}$  were suspended in 0.05M HEPES buffer (pH, 7.6).

was inhibited almost completely with 0.5 mM  $\text{Cd}(\text{NO}_3)_2$ . However, when DPC was added together with  $\text{Cd}(\text{NO}_3)_2$ , the kinetics of the fluorescence rise and the intensity at  $F_\infty$  were restored almost completely (Figure 95), confirming that the site of inhibition by Cd was before the DPC donating site. The above results were confirmed in five experiments.

(b) Absence of Inhibition on System I: P700

In untreated chloroplasts, PSI (729 nm) light caused an absorbance decrease of  $7.05 \times 10^{-4}$  at 703 nm (P700), while in the presence of 0.5 mM and 2.5 mM  $\text{Cd}(\text{NO}_3)_2$ , it was  $6.2 \times 10^{-4}$  and  $7.8 \times 10^{-4}$  respectively. The slight differences between the control and Cd treated chloroplasts are not significant. It is clear from these data that PSI activity is not sensitive to the concentrations of cadmium that inhibit water oxidation almost completely. This result was confirmed in three experiments.

(c) Effects of Pigments

(1) Absorption Spectra and Extraction of Pigments

Figure 3 shows the absorption spectra (630-750 nm region) of control (dashes and dots) and Cd treated (1 mM, 20 mins incubation; dashes only) chloroplasts containing about  $20 \mu\text{g Chl ml}^{-1}$  suspension; the solid curve represents an absorption spectrum of the control



but diluted to match the absorption at 660 nm with that of the Cd treated sample. The sample to which  $\text{Cd}(\text{NO}_3)_2$  was added reflected about 30% decrease in absorbance. Furthermore, the ratio of A678 (absorption at 678 nm, mainly due to Chl a) to A650 (mainly due to Chl b) is slightly higher (1.9) in the control than in the Cd treated sample (1.7). This difference (12%) was confirmed in all of the measurements on 20 different samples. It is clear that cadmium causes a decrease in the ratio of Chl a/Chl b, as shown by the difference absorption spectrum of Cd treated (dashed curve) minus control (solid line) chloroplast suspensions (see insert, Figure 96). This spectrum shows two small positive absorption bands at 695 nm (Chl a 695) and 645 nm (Chl a, Chl b?), and a large negative asymmetric broad band (half band width, 20 nm) at 677.5 nm (Chl a 670 and Chl a 680). These data further suggest that there has been a change in the ratio of short to long wavelength forms of Chl a.

The effect of different concentrations of Cd on A678/A650 showed a maximum decrease of 25% at 0.5 mM  $\text{Cd}(\text{NO}_3)_2$  which corresponds to 8  $\mu\text{M}$  Chl/50  $\mu\text{M}$  Cd. (The  $K_m$  of this effect was 8  $\mu\text{M}$  Chl/10  $\mu\text{M}$  Chl.) Furthermore, measurements

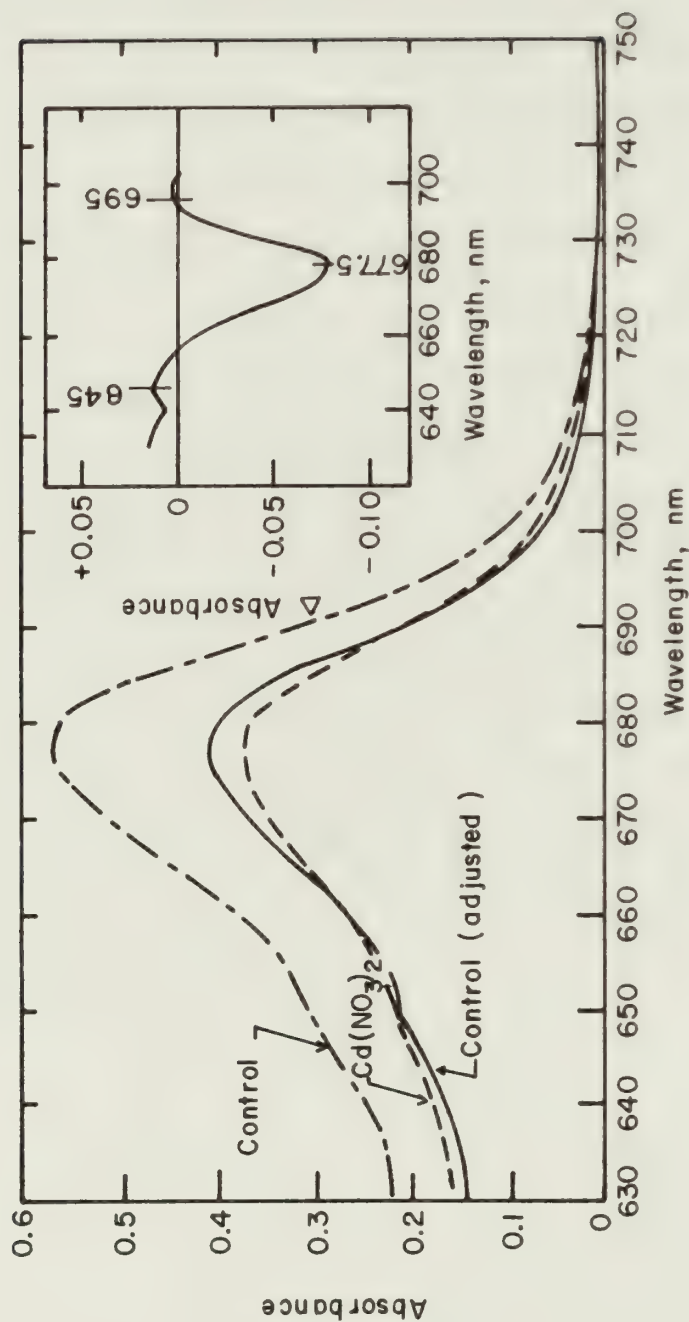


Figure 96

Absorption spectra of suspensions of control and Cd(NO<sub>3</sub>)<sub>2</sub> treated maize chloroplasts. (—) 20 µg chl ml<sup>-1</sup> (control); (---) 13 µg chl ml<sup>-1</sup> (control); (---) 20 µg chl ml<sup>-1</sup> with 1mM Cd(NO<sub>3</sub>)<sub>2</sub>. Inset: difference absorption spectrum of Cd treated (---) minus control (—) samples.

on the acetone extracts of untreated and Cd treated chloroplast suspensions showed that  $A_{678}/A_{650}$  of 1.9 (control) reflected Chl a/Chl b ratio of 4.2 (extract) while  $A_{678}/A_{650}$  of 1.7 (Cd treated) corresponded to Chl a/Chl b ratio of 1.6. A decrease of 42% in Chl a/Chl b ratio was thus obtained upon Cd treatment. Although these results show an actual decrease in ratio of Chl a/Chl b when  $\text{Cd}(\text{NO}_3)_2$  was added to chloroplasts, the absolute change may have been exaggerated if Cd complexed with some form of Chl a and, thus, did not permit its full extraction with 80% acetone.

## (2) Excitation Spectra of Chlorophyll a Fluorescence

Figure 97a shows the room temperature action (excitation) spectra for Chl a fluorescence at 740 nm ( $F_{740}$ ) for control and for Cd treated chloroplasts. The ratio of the intensity of fluorescence excited by Chl a (678 nm) to that by Chl b (650 nm) is lower in Cd treated sample in agreement with the results on  $A_{678}/A_{650}$  noted above. The intensities of fluorescence excited by wavelengths higher than 687 nm are higher in Cd treated samples, also in agreement with the results from the absorption spectra. The difference spectrum of the two excitation spectra shows two positive bands at 700 nm (Chl a 695) and 640 nm (Brody S. and Brody, M., 1963)

(Chl a, Chl b?) and a negative band around 680 nm (Chl a 670 and Chl a 680) (see Figure 97B). This results is similar to that of the difference absorption spectrum (insert, Figure 96) suggesting that cadmium does not elicit significant changes in the efficiency of excitation energy transfer. This is confirmed by the parallel decrease in Chl a absorption and fluorescence excited by 678 nm compared to the same for Chl b (650 nm). Experiments at 77°K showed similar results (not shown).

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#### IV. ANIMAL PROCESSES

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#### IV. Animal Processes

During the period covered by this report the following experiments were conducted and will be briefly presented in the following paragraphs:

1. A second long-term study on tissue accumulation and release of lead by adult male albino rats, combined with studies of lead intake in feed and excretion in feces and urine.
2. A study of the effects of dietary calcium and phosphorus on mobilization of previously accumulated lead in young male albino rats.
3. A preliminary study of possible metal co-factors affecting activity of ALAD.

##### Experiment 1

Methods - The general procedure was similar to that outlined in PR2, page 326, with the following variations. Dietary lead concentrations were designed to be 2, 50, 150, and 450 ppm. One hundred-sixty male rats of average initial weight about 350 grams were used. The following tissues from all animals were analyzed for lead content: tibia, blood, liver, kidney. In a few cases, other bones and residual carcasses were also analyzed for lead.

Results - There are no effects of the various dietary lead levels on the appearance, feed intake, weight gain or behavior of these animals. The tissue lead concentrations are shown in Table 39 and in general are confirmatory of the data reported in the two preceding progress reports. These data were obtained from 5 animals per treatment in each period. Table 40 shows results of lead analyses on skull, femur, vertebra, and tibia of 2 rats from each treatment and week during the period of lead dosage. It can be seen that lead concentration was least in skull, intermediate in femur and tibia and greatest in vertebra. The residual carcasses from rats used to provide data in Table 40 were analyzed for lead. Table 41 shows the micrograms of lead in each tissue and carcass and compares the total found with an estimate of lead intake obtained from the feed records. These data indicate that a very small portion of the lead supplement is retained in the tissues. The data have not been corrected for the lead originally present in the carcasses, thus the apparent high retentions of the "0" lead animals are not realistic. It is probable that these animals did not retain measurable amounts of their small intake of lead.

A 14-day collection of excretion was made from 5 rats on each treatment during weeks 7 and 8. Comparisons of

Table 39  
Lead Concentration in Tissues of Rats

Diet Pb (ppm)	Week	Lead Concentration (ppm fresh wt. $\pm$ S.E.)			
		Blood	Liver	Kidney	Tibia
0	Initial	.21 $\pm$ .08	.24 $\pm$ .04	.42 $\pm$ .04	.86 $\pm$ .18
	1	.56 $\pm$ .16	.58 $\pm$ .08	.66 $\pm$ .12	1.74 $\pm$ .52
	2	.34 $\pm$ .05	.23 $\pm$ .04	.70 $\pm$ .13	3.11 $\pm$ .13
	4	.22 $\pm$ .01	.18 $\pm$ .01	<.7	<.8
	8	.10 $\pm$ .02	.15 $\pm$ .02	<.6	.94 $\pm$ .10
	9	.19 $\pm$ .03	.20 $\pm$ .01	.84 $\pm$ .29	1.80 $\pm$ .11
	10	.24 $\pm$ .06	.22 $\pm$ .04	.98 $\pm$ .27	1.80 $\pm$ .14
	12	.22 $\pm$ .06	.22 $\pm$ .02	.44 $\pm$ .04	.85 $\pm$ .10
	16	<.33	.19 $\pm$ .02	.29 $\pm$ .01	1.22 $\pm$ .12
50	1	.41 $\pm$ .06	.33 $\pm$ .06	4.6 $\pm$ .7	5.5 $\pm$ 1.2
	2	.52 $\pm$ .08	.78 $\pm$ .15	5.1 $\pm$ 1.2	15 $\pm$ 2
	4	.35 $\pm$ .13	.51 $\pm$ .05	3.7 $\pm$ .3	13 $\pm$ 1
	8	.14 $\pm$ .02	.27 $\pm$ .04	1.6 $\pm$ .3	6.6 $\pm$ 1.8
50-0*	9	.21 $\pm$ .03	.23 $\pm$ .02	1.3 $\pm$ .2	12 $\pm$ 3
	10	.21 $\pm$ .03	.22 $\pm$ .01	1.5 $\pm$ .2	8.9 $\pm$ 1.4
	12	.29 $\pm$ .08	.27 $\pm$ .03	1.0 $\pm$ .2	9.0 $\pm$ 2
	16	<.33	.23 $\pm$ .02	.81 $\pm$ .10	8.2 $\pm$ .6
150	1	.51 $\pm$ .04	1.2 $\pm$ .1	7.6 $\pm$ .6	14 $\pm$ 2
	2	.55 $\pm$ .07	1.1 $\pm$ .2	9.1 $\pm$ 2.3	28 $\pm$ 6
	4	.45 $\pm$ .06	.50 $\pm$ .11	5.0 $\pm$ 1.4	29 $\pm$ 6
	8	.26 $\pm$ .04	.55 $\pm$ .07	3.1 $\pm$ .3	26 $\pm$ 5
150-0*	9	.42 $\pm$ .09	.36 $\pm$ .03	3.0 $\pm$ .6	24 $\pm$ 3
	10	.42 $\pm$ .10	.32 $\pm$ .02	2.0 $\pm$ .2	23 $\pm$ 4
	12	.22 $\pm$ .04	.31 $\pm$ .03	2.1 $\pm$ .09	24 $\pm$ 2
	16	<.33	.31 $\pm$ .05	1.7 $\pm$ .3	17 $\pm$ 4
450	1	.75 $\pm$ .09	2.0 $\pm$ .2	33 $\pm$ 5	32 $\pm$ 2
	2	.65 $\pm$ .11	1.7 $\pm$ .3	16 $\pm$ 4	49 $\pm$ 7
	4	.55 $\pm$ .04	1.5 $\pm$ .3	12 $\pm$ 4	53 $\pm$ 8
	8	.44 $\pm$ .08	1.6 $\pm$ .4	12 $\pm$ 4	68 $\pm$ 20
450-0*	9	.31 $\pm$ .04	.73 $\pm$ .09	7.0 $\pm$ 1.7	65 $\pm$ 13
	10	.46 $\pm$ .04	.55 $\pm$ .06	5.4 $\pm$ 1.1	66 $\pm$ 10
	12	.38 $\pm$ .06	.53 $\pm$ .06	4.1 $\pm$ 1.0	56 $\pm$ 9
	16	<.33	.45 $\pm$ .05	4.1 $\pm$ .6	57 $\pm$ 8

\*Animals given no lead supplement after week 8.

Table 40  
Concentration of Lead in Separate Rat Bones  
(ppm Pb in Bone Ash)

<u>Week</u>	<u>Diet Pb (ppm)</u>	<u>Skull<sup>1</sup></u>	<u>Femur<sup>1</sup></u>	<u>Vertebra<sup>1,3</sup></u>	<u>Tibia<sup>2</sup></u>
1	0	.6	2	3	3
	50	5.6	18	28	17
	150	13	33	40	38
	450	32	90	100	78
2	0	.4	1	.6	6
	50	13	37	52	34
	150	26	78	105	67
	450	61	134	147	144
4	0	.5	1	2	2
	50	14	36	48	33
	150	56	147	200	98
	450	81	198	249	149
8	0	2	6	6	2
	50	6	16	19	10
	150	46	84	119	73
	450	92	195	262	154

<sup>1</sup>Data from 2 animals treatment and period

<sup>2</sup>Data from 5 animals treatment and period

<sup>3</sup>8-10 vertebra removed

Table 41  
Micrograms Lead Per Tissue Or Organ Removed

Week	Diet Pb (ppm)	Liver	Kidney	Skull	Femur	Tibia	Vertebra	Blood	Carcass Residue	Total Pb Found (mg)	Total Pb Intake (mg)	% of Intake Found
1	0	8.5	2.1	1.1	1.2	2.7	2.1	2.6	148	.17	.26	65
	50	2.6	13	10	12	11	15	3.0	325	.39	8.5	5
	150	16	14	22	22	24	31	3.0	517	.65	21	3
	450	22	73	51	56	51	82	5.7	550	.89	68	1
2	0	4.5	1.2	.7	.7	5.8	.7	1.2	177	.19	.53	59
	50	10.2	14	23	28	26	28	3.2	507	.64	15.8	40
	150	15	18	43	55	44	57	3.7	665	.90	48	40
	450	18	47	93	80	93	110	3.3	1612	2.06	136	40
4	0	2.5	1.8	1.2	1.2	1.6	1.3	1.3	150	.13	1.3	10
	50	8.3	10	28	30	23	36	3.0	356	.49	33	10
	150	9.0	18	110	110	71	110	1273	1273	1.70	93	10
	450	23	26	165	160	125	215	1886	1886	2.60	290	1
8	0	2.5	1.5	5.0	5.9	1.6	5.3	5.3	111	.13	2.0	7
	50	3.0	3.4	14	16	8.5	19	19	175	.24	71	7
	150	9.0	11.0	119	86	71	130	130	1013	1.44	215	1
	450	18	39	195	185	135	170	2561	2561	3.30	785	1



lead intake with fecal and urinary lead showed that 86% of the added lead was excreted regardless of the lead intake; 2% of the excretion was via urine. The linear correlation between intake and outgo of supplemental lead was 0.988. The value of 86% excretion is lower than that of 95% reported in on page 182 PR3. This may be accounted for by the fact that the rats in the present experiment were younger and accumulated more lead in their skeletons than those in the previous experiment.

Table 42 shows results of measurements of amino-levulinic acid dehydrase (ALAD) activity in blood during lead dosage and recovery. A clear effect of the different lead dosages is seen. Even after 8 weeks of recovery on the "0" lead diet ALAD was markedly depressed in blood of the rats previously fed 450 ppm. More than 4 weeks of recovery were required for a clear response in ALAD in the group previously fed 150 ppm.

#### Experiment 2

Methods - Eighty 100-gm male rats were divided into 2 equal groups and fed either "0" or 300 ppm supplemental lead in our usual purified diet with normal (0.7%, 0.5%) calcium and phosphorus for 3 weeks. Ten animals were killed at the end of this period. The remaining animals

Table 42  
Blood Aminolevulinic Acid Dehydrase Activity\*

<u>Week</u>	<u>Dosage (ppm Pb)</u>			
	<u>0</u>	<u>50</u>	<u>150</u>	<u>450</u>
1	141+7	30+5	14+3	10+4
4	118+14	31+7	40+11	9+2
9**	200+15	117+13	68+3	28+7
10	169+6	128+10	74+6	19+2
12	198+6	188+28	89+4	48+7
16	250+25	201+26	151+28	32+4

\* $\mu$ M ALA used/min/mg blood  $\times 10^{-8}$

\*\*All animals placed on "0" lead diet at end of week 8.

were continued on their previous lead treatment but, in groups of 10 were given (a) normal Ca and P, (b) low Ca (0.2%) normal P (.5%), or (c) normal Ca (.7%) high P (1.8%). These treatments were continued for six weeks, with 5 animals/treatment (total of 30) killed after 1 (week 4) and six (week 9) weeks. Tissue analyses for lead, ALAD and calcium were made with results as shown in Tables 42 and 43.

Results - Lead content of the tissues analyzed was clearly elevated by lead treatment, particularly in animals receiving the low calcium diet. High phosphorus in presence of normal calcium did not alter lead accumulation from that obtained in the normal Ca-P diet. The same trends are seen in blood ALAD: a large effect of lead in decreasing ALAD which was somewhat exaggerated by the low calcium treatment with respect to the other two treatments. (Table 44 )

### Experiment 3

Methods - In this initial study of factors affecting activity of ALAD a partial purification of the enzyme from rat liver was accomplished. It was found that the ability of this preparation to convert aminolevulinic acid to porphobilinogen was markedly enhanced by addition of

Table 43  
Lead Concentration (ppm fresh basis) in Rat Tissues  
As Affected By Lead, Calcium, and Phosphorus

			Week 3			Week 4			Week 9		
			Blood	Kidney	Tibia	Blood	Kidney	Tibia	Blood	Kidney	Tibia
Ca	P	Pb									
N	N	-	.28±.02	.9±.2	1.01±.09	.23	.98±.08	1.1±.06	.3±.04	.8±.07	.9±.1
L	N	-				.23	.56±.10	1.2±.18	.3±.04	1.0±.17	1.2±.3
N	H	-				.23	.68±.10	1.1±.11	.2±.03	.7±.04	.8±.1
N	N	+	.57P.03	7.0±.4	45±3	.6±.10	5.7±.5	51±2	.3±.05	7.3±.6	56±6
L	N	+				.7±.04	14.7±.9	57±6	.55±.08	25±4	111±15
N	H	+				.6±.02	3.8±.4	30±4	.35±.07	6.6±1	53±7

Table 44

Blood ALAD as Affected by Lead, Calcium and Phosphorus

Treatment			<u>Week 3</u>	<u>Week 4</u>	<u>Week 9</u>
<u>Ca</u>	<u>P</u>	<u>Pb</u>			
N	N	-	395+ <u>29</u>	346+40	263+22
L	N	-		353+29	196+22
N	H	-		294+ <u>25</u>	162+ <u>21</u>
N	N	+	60+ <u>3</u>	24+10	11+1
L	N	+		15+3	3+3
N	H	+		45+ <u>6</u>	14+ <u>6</u>

zinc to the reaction medium after inactivation by EDTA.  
Other divalent cations tested were ineffective.



## Lead Metabolism and Toxicity during Chronic Ingestion in the Pregnant and Fetal Guinea Pig

The broad objective of this experiment was to study lead metabolism in the pregnant, fetal and neonated guinea pig. The immediate objectives were: (1) to produce steady-state blood concentrations of lead by continuous oral ingestion in female guinea pigs and to measure lead transfer to the fetus at several stages of pregnancy during the maternal steady-state condition, and (2) to determine tissue concentrations of lead in dam and fetus and the relative sensitivities of maternal and fetal tissue to such concentrations by observations of signs of functional impairment and histopathologic techniques. Because support for this project was available for a shorter time interval than anticipated, only one experiment was performed with the objective of measuring tissue concentrations at the end of gestation.

### Methods

Twenty-four sexually mature, nonpregnant female guinea pigs were placed in metabolism cages. Six animals were fed each of the following diets containing (1) no added lead (control) and lead acetate to provide concen-

trations of (2) 500 ppm, (3) 1000 ppm, and (4) 2000 ppm. Blood samples were obtained from all animals on alternate weeks and males were placed with each female after four weeks of feeding on lead diets after maternal blood lead concentrations had reached approximate steady states. The males were removed seven weeks later.

It was intended that pregnant females should proceed to delivery, at which time dam and fetuses were to be killed and tissues taken for histologic sectioning and lead analysis. As explained in the following "results" section, technical complications prevented the execution of this format with the exception of a few animals. Blood and tissue lead concentrations were measured by atomic absorption spectrometry in the analytical laboratory. Histopathologic examination is to be performed by light microscopy in the Department of Pathology and Hygiene, College of Veterinary Medicine.

### Results and Discussion

Blood lead concentrations reached a plateau after about 4 to 5 weeks of feeding the four diets, with final concentrations after 3 months increasing in direct, although not linear, proportion to the dietary concentrations

(Table 45). Both the survival and pregnancy rates of maternal animals were lower than desired, primarily because of a suspected viral pneumonia in the colony during the experiment. The animals were accustomed to solid bottom cages, and we strongly suspect the wire bottom metabolism cages of causing sufficient stress to induce an indigenous virus to become active. As a consequence, the entire 3-month experiment was completed by only two of the control animals, none of the 500 ppm group (although 5 survived two and one-half months), 4 of the 1000 ppm group, and 4 of the 2000 ppm group. Both the post-mortem results and higher survival rates in the high-lead dietary groups suggest that the death losses were caused by cage stress and an infectious agent rather than by lead toxicity.

Tissue concentrations of lead (Table 46) in the control females were of the same order of magnitude as their blood lead concentrations; but as dietary lead was measured, tissue lead far exceeded blood lead. The general pattern in maternal tissues, from highest to lowest concentration, was: bone > liver > kidney > brain > uterus. The most interesting finding was the extremely high build-up of lead in fetal bone, to as much as 8-10 times the concentration found in maternal bone of the

Table 45

Maternal Blood Lead Concentrations during Feeding (ppm)								
<u>Bleeding Date:</u>	<u>5/5/73</u>	<u>5/26/73</u>	<u>6/1/73</u>	<u>6/15/73</u>	<u>6/29/73</u>	<u>7/13/73</u>	<u>7/27/73</u>	<u>8/10/73</u>
<u>Group:</u> Control	.34(6)*	.48(6)	.47(6)	.21(5)	.36(5)	.18(4)	.53(2)	.72(2)
500 ppm	.33(6)	.87(6)	1.52(6)	1.07(6)	1.10(6)	.78(5)	.85(5)	-
1000 ppm	.38(6)	.85(5)	1.10(6)	.96(6)	.79(6)	.97(5)	1.14(5)	1.17(4)
2000 ppm	.53(6)	.95(5)	.74(6)	1.11(6)	1.04(6)	1.52(6)	1.28(6)	1.38(4)

\*Number of guinea pigs bled shown in parentheses. Blood lead concentration is the average of the concentrations for that group of animals.

Table 46

Maternal and Fetal Tissue Concentrations of Lead (ppm in Wet Tissue)

<u>Dietary Group</u>	<u>Tissue</u>			
	<u>Brain</u>	<u>Femur</u>	<u>Kidney</u>	<u>Liver</u> <u>Uterus</u>
Control Maternal	.10	.014	.10	.21 .27
Fetal(6)*	.52	56.9	1.83	1.42 11.6
500 ppm Maternal	2.1	32.2	3.46	3.23 1.05
Fetal(1)	.95	250	1.19	16.8 -
1000 ppm Maternal	1.8	219	4.5	5.7 1.5
Fetal(3)	.67	3,372	1.8	6.0 3.4
2000 ppm Maternal	81	626	7.8	19 1.3
Fetal(6)	1.3	5,700	2.6	3.8 39

\*Number of fetuses from which tissues were analyzed. Only fetuses at or near term gestation were included.

same dietary group. This observation might very well be expected, considering the highly active state of mineralization and turnover in fetal bone which would lead to efficient extract of lead from fetal blood. It also suggests there is no significant placental barrier to lead transfer in this species. An important side effect of the avaricious retention of lead by fetal bone appears to be a concurrent reduction of fetal soft tissue lead. Lead concentrations in fetal brain and kidney were one-half their respective concentrations in the same maternal tissues, whereas fetal liver concentrations were both higher and lower than maternal values. Uterine lead values for the fetus are of doubtful significance, the tissue mass being so small that the total lead was below the detection limit of the analytical method following ashing and dilution. Histopathologic examination of tissue sections has not been completed at this time, but will be during the summer.



## V. MODELING

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## V. Modeling

### Distribution Models

#### A. The Watershed Model

The total ecosystem model was developed to simulate lead movement throughout the watershed and to predict lead accumulation in the various components of the ecosystem. The model is simulated in time steps of one week. For convenience, a year is composed of 13 months of four weeks. The model contains 35 nodes connected by 132 branches. Each week 4632 grams of lead is assumed to be emitted per  $\text{Km}^2$ . The model distributes this lead to various nodes and then re-distributes the lead contained in the nodes. The flow from node  $i$  to node  $j$  is computed as follows Rolfe, et al.(1972):

$$(1) \quad y_{ij}(t) = x_i(t) \left( \frac{d_{ij} \cdot s_{ij}(t)}{\sum_{j=1}^n d_{ij} \cdot s_{ij}(t)} \right)$$

where:  $y_{ij}$  is the quantity of lead moving from node  $i$  to node  $j$

$x_i$  is the quantity of lead in node  $i$

$d_{ij}$  is the flow, relative to other branches leaving  $i$ , from  $i$  to  $j$

$n$  is the number of branches leaving a node

$s_{ij}$  - a seasonal factor for branch  $ij$  at time  $t$ . The seasonal factor is a step function to simulate a non-linear function such as plant or animal growth. Each function is divided into 13 steps of four weeks each. The quantity of lead present in node  $i$  at time  $t$  is:

$$(2) \quad x_i(t) = x_i(t-1) + y_{ji}(t) - \sum_{j=1}^n x_i(t-1) \cdot \left( \frac{d_{ij} \cdot s_{ij}}{\sum_{i=1}^n d_{ij} \cdot s_{ij}} \right)$$

The model is composed of two units, the terrestrial and aquatic subsystems. The terrestrial subsystem is further divided into four zones as explained in the ecosystem section. Figure 98 gives the nodes and branches of zone I, along with relative atmospheric inputs to zones II, III, and IV.

The decimal values are the  $d_{ij}$ 's of equations 1 and 2. The numbers in parentheses refer to seasonal factors  $s_{ij}$  listed in Table 47. Zones III and IV differ in that the pavement node is absent in III and the pavement node in IV is assumed to be connected to storm sewers so that 40% of the lead enters the surface water rather than 10% as in zones I and II. The relative inputs into the zones per week are: Zone I (13%), Zone II (3.8%), Zone III (.4%) and Zone IV (72.6%); 10.2% remains airborne. The majority of the

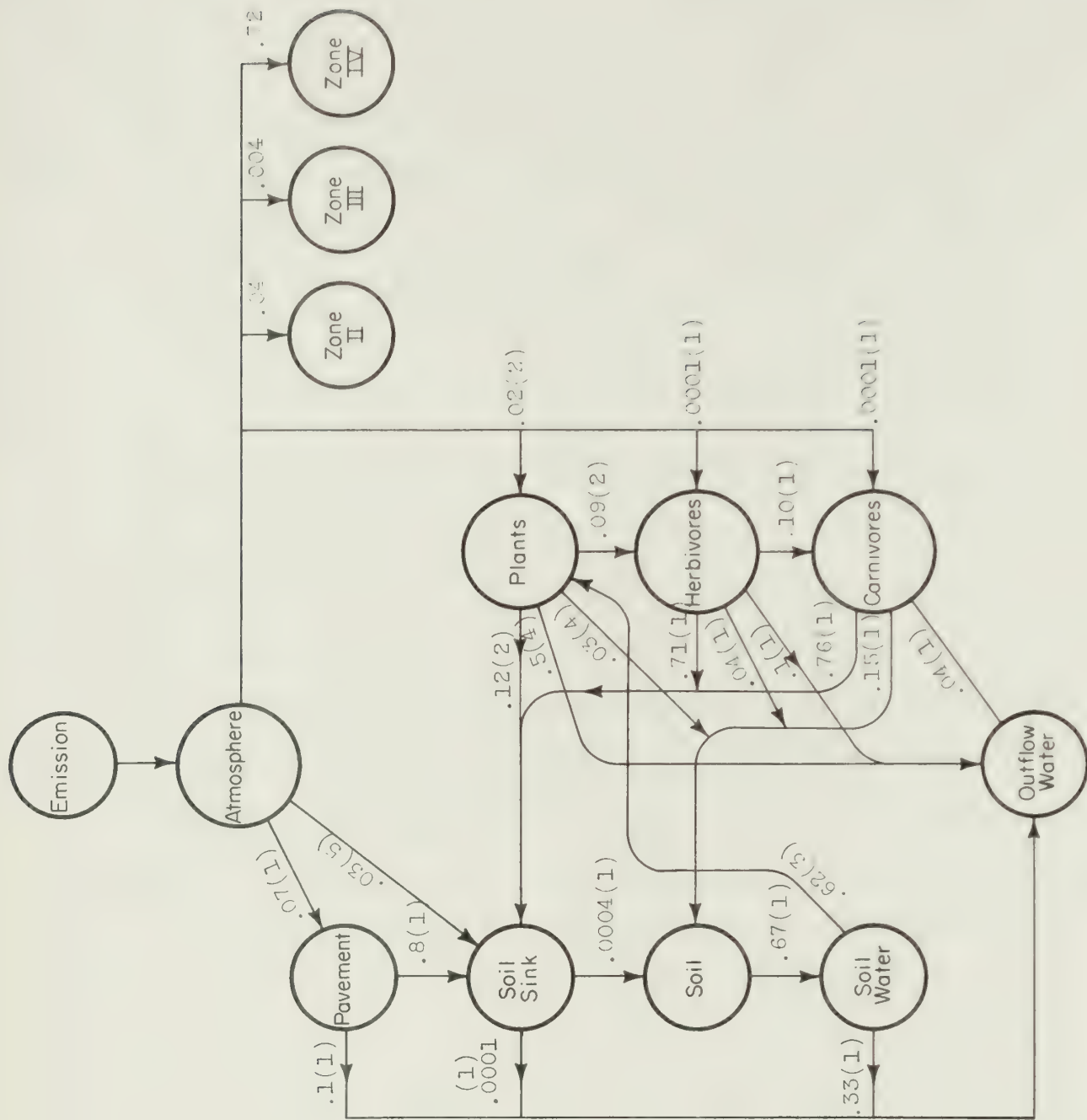


Figure 98

The nodes and branches of Zone I. Decimal values are relative flows between nodes, numbers in parentheses are seasonal factors.

Table 47

Seasonal factors used in computation of relative flows

Seasonal Factor	Time Period*												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.
2	1.6	1.6	1.5	1.16	.78	.63	.48	.48	.48	.62	.89	1.3	1.54
3	2.5	2.5	2.1	1.	.21	0.	0.	0.	0.	.22	.64	1.64	2.3
4	.8	.8	.99	1.55	1.91	1.31	.8	.8	.8	.8	.8	.8	.8
5	.43	.43	.57	.93	1.16	1.29	1.43	1.43	1.43	1.3	1.06	.69	.49

\*Time periods are four weeks. Time period 1 begins July 1.

lead (72.6%) is deposited in the urban system. The terrestrial and aquatic subsystems are linked through the surface water. The nodes and branches for the aquatic subsystem are given in Figure 99.

The ecosystem model has been used to estimate the change in lead concentration since the introduction of leaded gasoline (assumed to be in 1924). The yearly estimated consumption of gasoline is consumed from traffic counts and estimated lead content from 1947 to 1972 was taken from U.S.B.M. Mineral Industry Surveys, "Petroleum Product Surveys". The average lead concentration in gasoline in 1924 is assumed to be .5 gram per gallon and to increase at a rate of .1 gram per gallon to a level of 1.7 gram in 1935. The lead content between 1935 and 1947 is assumed to remain constant.

The precision of the estimate of lead content in this early period, 1924-1947, is not critical to the simulation as total gasoline consumption was low. The results of this simulation are given in Table 48. For convenience, soil water, soil sink, and soil are grouped under the heading of soil.

During the simulation period an estimated 1,100 tons of lead has been released into the watershed. The majority



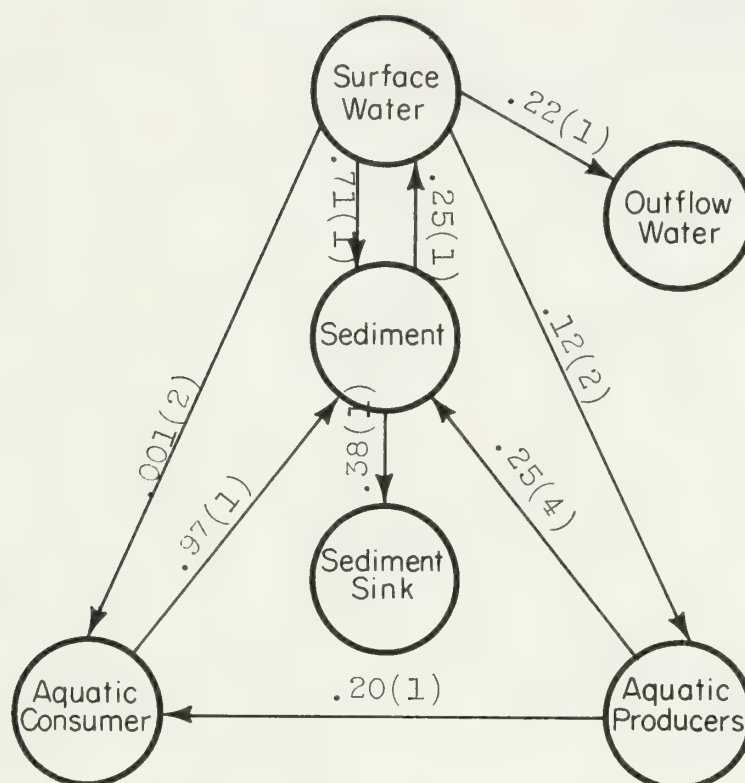


Figure 99

The nodes and branches of the aquatic subsystem. Decimal values are relative flows between nodes, number in parentheses are seasonal factors.

Table 48

Estimated change in lead concentrations in components in 1972.  
Simulation Period is from 1924 to 1972.

Zone	Component	Lead Concentration	Units
Terrestrial Subsystem			
I	Pavement	1800	ug/m <sup>2</sup>
	Soil	78	ppm
	Plants & Litter	15	ppm
	Herbivores	20	ppm
	Carnivores	10	ppm
II	Pavement	300	ug/m <sup>2</sup>
	Soil	10	ppm
	Plants & Litter	2	ppm
	Herbivores	5	ppm
	Carnivores	1	ppm
III	Soil	<1	ppm
	Plants & Litter	<1	ppm
	Herbivores	<1	ppm
	Carnivores	<1	ppm
IV	Pavement	5400	ug/m <sup>2</sup>
	Soil	230	ppm
	Plants & Litter	110	ppm
	Herbivores	70	ppm
	Carnivores	30	ppm

Table 48 continued

Aquatic Subsystem			
Zone	Component	Lead Concentration	Units
	Surface water	1	ppm
	Outflow water	1	ppm
	Aquatic producers		
	Aquatic consumers		
	Sediment Sink	20	ppm

of the lead, 70%, is contained within the soil. The sediment sink contains 19% of the emitted lead; 10% has left the system via the outflow water. The other 1% is distributed through the remaining compartments.

The ecosystem model has been used to simulate future lead levels for the next 10, 50, and 100 years using different emission control strategies. The estimated levels in Table 47 serve as initial conditions for the future predictions. An average gasoline content of 2.5 gram of lead per gallon and a consumption growth rate of 3% are assumed. Since the simulations are based on emission level, the results should be the same if the lead content of gasoline is reduced or if a control device is added. The initial effect of a reduction in lead content would be more pronounced since control devices would probably only affect new cars.

The estimated values for the future simulation are given in Table 48. As in the previous table the values are above background levels. The values in the column for 100% reduction in emissions demonstrate the slow release of lead from the system. After 10 years the soil levels will have decreased about 2% and the plants about 33%. If no controls are made, soil levels will increase approximately 33% and plants about 40%.

At this time it is not certain if gasoline will be available for the next 50 or 100 years. If leaded gasoline is used for this length of time, the need for concern is obvious from Table 49. Even with a 50% reduction in lead emissions, the soil and plant concentrations of Zones I and IV will be dangerously high in 50 years.

#### Roadside Model

Zone I of the ecosystem model was modified to estimate the lead accumulation in soils and vegetation of five 10m strips along a highway. The model is composed of five units similar to that shown in Figure 49. They differ however, in that: (1) the herbivore and carnivore nodes and seasonal factors are not included; (2) the output from one strip is through the soil water and serves as input to the soil water of an adjacent strip; (3) only the soil water of the fifth section is connected to the surface water; and (4) the branch of the pavement to the surface water flows to the soil water of the first strip.

The model assumes an emission rate of .108 gram of lead per vehicle mile, of which 50% remains airborne, Cantwell, et al. (1973). Twenty five percent of the lead is assumed to settle on the pavement. The remaining 25% is distributed to the five strips as follows: 0-10 (12%), 10-20 (6%),

Table 49

The Effects of Four Emission Control Strategies on Lead Levels. The Time Period Begins in 1972. Figures are ppm Above Background Levels.

YEARS	NODE	ZONE				
10	Soil	I	115	102	89	63
		II	17	15	13	10
		III	<1	<1	<1	<1
		IV	315	283	250	190
	Plants	I	37	30	23	10
		II	15	4	3	1
		III	<1	<1	<1	<1
		IV	256	209	163	71
50	Soil	I	450	345	239	29
		II	68	52	36	4
		III	1	1	1	<1
		IV	1095	834	591	89
	Plants	I	132	100	68	5
		II	19	14	10	1
		III	<1	<1	<1	<1
		IV	868	659	450	33
100	Soil	I	2062	1549	1037	14
		II	313	235	157	4
		III	6	5	3	<1



Table 49 continued

	V	4941	3714	2487	78
Plants	I	597	449	300	<1
	II	85	64	43	<1
	III	2	2	1	<1
	IV	3903	2930	1958	<1

20-30 (3%), 30-40 (2%), 40-50 (2%). The internal distribution follows that of Zone I.

The model was simulated for one and four years. The results for 10,000 and 50,000 vehicle miles per day are listed in Table 50.

Since the seasonal factors have been omitted, the lead concentration is a linear function of vehicles per day. Concentrations for the other daily traffic volumes can be estimated from the data in Table 50. For example, a traffic volume of 25,000 vehicles per day would give an estimated concentration of 14ppm lead in the soil of the 0-10 meter zone after one year. The concentration for a given traffic volume is linear with time after the first few weeks. Thus, concentrations at other times can also be estimated. For 25,000 vehicles per day after five years, the estimated soil concentration in the 0-10 meter zone would be:

$$118 + \left(\frac{118-28}{3}\right) = 148\text{ppm}$$

Table 50

Predicted increase in lead concentration of roadside vegetation  
and soil.

Distance from pavement, meters		Vehicles per day			
		10,000 1 year	4 year	50,000 1 year	4 year
		ppm Lead			
0-10	Soil	6	23	28	118
	Vegetation	43	63	215	318
10-20	Soil	1	5	5	24
	Vegetation	20	30	98	152
20-30	Soil	.5	2	3	11
	Vegetation	9	14	45	71
30-40	Soil	.3	1	1	6
	Vegetation	4	7	22	35
40-50	Soil	.3	1	1	6
	Vegetation	3	5	16	25

## B. Highway Fuel Consumption Model

### Introduction

Estimates of highway fuel consumption within a defined watershed system may be obtained through the use of a carefully planned traffic monitoring program within the study area. Such data, however, are not available in all geographic or temporal settings. Even where limited data are available, the information is unlikely to coincide with the boundaries of the ecosystem under consideration. A study area may well have combinations of rural and urban sectors with different vehicle operating characteristics and growth rates; or travel in the defined area may even be influenced more by major activity centers which are actually outside the immediate study boundaries. Thus, there is an obvious need to study existing relationships between vehicular travel and other land use, population and socio-economic variables to develop estimates of automotive lead emissions where traffic monitoring has not been done in the past or would be impractical in the future.

For the Saline Branch Watershed study two aspects of vehicular travel were of particular concern. First, to improve our understanding of the movement of lead through

the plant, animal, soil and water subsystems, the historical distribution of lead emission was desired to improve modeling procedures which assume initial lead concentrations of zero in the subsystems. Secondly, current distribution of travel was needed for developing other ecosystem models such as the atmospheric model. Based on these concerns the objectives of the transportation modeling group have been to:

1. Obtain historical records of travel and other variables which are related to traffic growth.
2. Evaluate aggregate national, state, and local data and consider general models which could be used to estimate historical lead output in the Saline Branch with a view to having these procedures transferable to other areas.
3. Examine study area socioeconomic and demographic characteristics which might be used to estimate trip volumes on major links of the existing network.

#### Data Sources

Travel data, fuel consumption figures, population characteristics, roadway mileage and other variables which may be related to lead emissions are available at several levels of geographic data aggregation and for different periods of time. The data sources discussed below were

examined during the study of the Saline Branch Watershed and would likewise be generally available for analysis of other ecosystems.

National Level - On a national scale the federal agency responsible for highway development, currently the Federal Highway Administration, publishes annual estimates of highway route mileage, vehicle miles of travel, vehicle registrations, and highway fuel consumption, Annual Report of HIGHWAY STATISTICS, Federal Highway Administration, 1971. Vehicle registration and highway fuel consumption figures are available from 1925, the approximate time that leaded gasoline was introduced. The national report also contains breakdowns of each of these variables for individual states.

Population characteristics which may be related to travel demand can be obtained from U.S. Census reports at even finer levels of spatial aggregation, i.e., by state, county, city, census tract or even by city block for SMSA's of the most recent census. These data are of course available only at ten year increments.

State Level - Records of travel trends within the State of Illinois were obtained from annual reports of the Division of Highways, 1972. Limited vehicle count data were available from selected rural road counting stations around



the study area dating to 1941. More extensive periodic counting programs provide the basis for county traffic maps which are revised about every six years. These maps, available since the early 1950's, provide greater detail on primary and secondary routes within the rural area. Similar programs within urban areas provided traffic flow data for the major street network of Champaign-Urbana.

Vehicle registration data were available from the State Motor Vehicle Division for Champaign County since 1945.

Municipal Level - The most important source of travel data within the Champaign-Urbana metropolitan area is the C-U transportation study which is a major planning study performed in cooperation with the state and federal governments. Studies conducted in 1958 and 1965 provide the greatest detail of total trips within the study area as well as traffic approaching the city, Champaign-Urbana Urban Area Transportation Study (CUATS) Final and Interim Reports, 1970; State of Illinois Department of Public Works and Buildings, Traffic Survey, Champaign-Urbana Urban Area, 1958. A 1948 study provided additional information on traffic approaching the city, State of Illinois Department of Public Works and Buildings, A Study

of Traffic in the Vicinity of Champaign and Urbana, Illinois,  
1948. The 1965 study is of additional value in that vehicle ownership, employment and population data are summarized by smaller traffic zones within the urban area. These data had been thoroughly evaluated and forecasting equations developed to estimate the number of vehicle trips expected in the target year, 1985.

#### Data Analysis - Historical Record

Since the most complete historical record of fuel consumption was available at the national and state levels, these data were first examined to guide the efforts in estimating fuel consumption. Figure 100 shows the historical trend between highway fuel consumption, vehicle registrations and population. To evaluate the statistical strength of these relationships, linear regression models were developed at both the national and state level using all years from 1925 except for six years during the depression and World War II. At each analysis level, a model using vehicle registration as the independent variable would appear to explain 99 percent of the variation in highway fuel consumption. Although suggesting that vehicle registrations at the county or metropolitan area would provide an excellent basis for estimating consumption

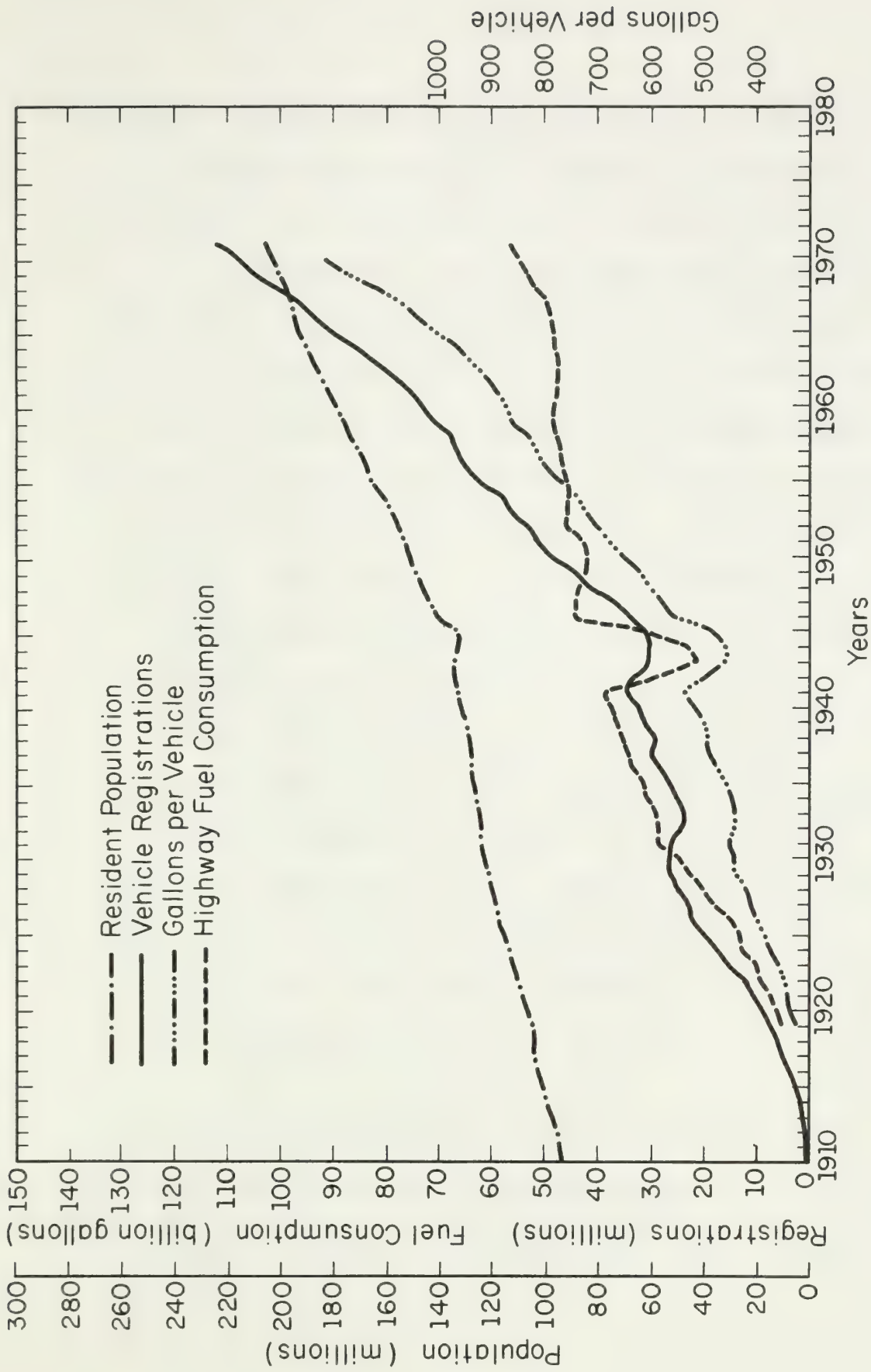


Figure 100  
National Trends of Travel Related Variables

within the smaller watershed area, these regression equations should not directly be used in a smaller area because the character and rate of growth in the smaller area may be quite different than state averages. For example, within the State of Illinois approximately 60 percent of the travel occurs on urban roads, State of Illinois, Fifty-Third Annual Report, 1970, whereas the monitoring team reports that 80 percent of the travel is within the defined urban compartment of the Saline Branch Watershed.

Urban Compartment Analysis - Several approaches were evaluated for estimating fuel consumption in the urban area. In all initial modeling efforts, the single consumption estimate developed by the traffic monitoring group for 1971 served as the base point through which historical curve estimates passed. Although this figure was considered to be the most accurate estimate possible due to the special planning directed specifically to the watershed study, additional estimates were later made for earlier years using the Division of Highways traffic volume maps.

In addition to the significance of vehicle ownership cited above for national and state data, the Champaign-Urbana Area Transportation Study (CUATS) found vehicle

ownership within the metropolitan area to be the most important variable to explain urban trip production variations. The first consumption estimates were therefore based on the simple allocation of the total county vehicle registrations to the watershed area and the application of statewide consumption figures to those vehicles. Other estimates using vehicle registration adjusted the average figures by accounting for the effect of different operating characteristics on urban and rural roads and the resultant effect on consumption rates.

A second major modeling approach recognized that fuel consumption in the urban areas is a function of the number of trips produced and the average trip length. Voorhees et al., 1968, modeled the average trip duration of selected trip types in terms of city population. Their model, which was based on data from cities ranging from 10,000 to 10,000,000 population, was of the form  $t = \alpha P^\beta$

where

$t$  = trip duration in minutes

$P$  = urban population, and

$\alpha, \beta$  are constants

Trip length data from the CUATS were used to calibrate a similar model for the C-U study area. The C-U travel



studies and the Division of Highways traffic volume maps were also used to provide an indicator of the total number of trips in the area so vehicle mile estimates could be made.

The fuel consumption estimates obtained from the above models were checked by comparing with estimates derived from urban area traffic maps of 1956, 1962 and 1968. The comparisons indicated that the models based on average trip length and C-U transportation studies would provide the best consumption estimates. These models, however, still do not provide an adequate means for estimating lead output prior to the time when actual traffic data were available. Since population data are the only figures available for the urban area dating back to the 1920 period, population growth of the urban area is felt to be the best indicator of long term travel growth.

The vehicle mile estimates obtained from traffic maps and census data were used to estimate vehicle-miles of travel since 1920. The general form of the model was:

$$V-M = \alpha P^{\beta} \text{ where}$$

V-M = vehicle-miles of travel in the urban compartment of the Saline Branch Watershed, in thousands;

P = population of Champaign and Urbana, in thousands and  $\alpha$  and  $\beta$  are constants.



For the study area considered in this analysis,  $\alpha = 0.04$  and  $\beta = 2.11$ . The correlation coefficient was 0.86.

Figure 101 shows the projected travel estimates.

Rural Compartment Analysis - Travel growth studies in areas around major urbanized areas are generally based on the premise that the number of trips undertaken is a function of the growth of the major activity centers and the accessibility to those centers. Previous research efforts by Jones have demonstrated that the number of trips passing through a cordon line around an urbanized area is dependent upon such factors as county vehicle registrations, county population density, metropolitan population and employment opportunities, Jones, 1972. Of all the parameters considered for the Saline Branch Watershed, county vehicle registration and county population appeared to be the better indicators of travel. Vehicle registrations again, however, are incomplete through the time period of interest. A population--vehicle miles of travel curve similar to Figure 101 was therefore established for the rural area. Because of the more extensive nature of the study by Jones, his results may be more applicable for determining corridor movements in other watershed areas if satisfactory data sets are available.

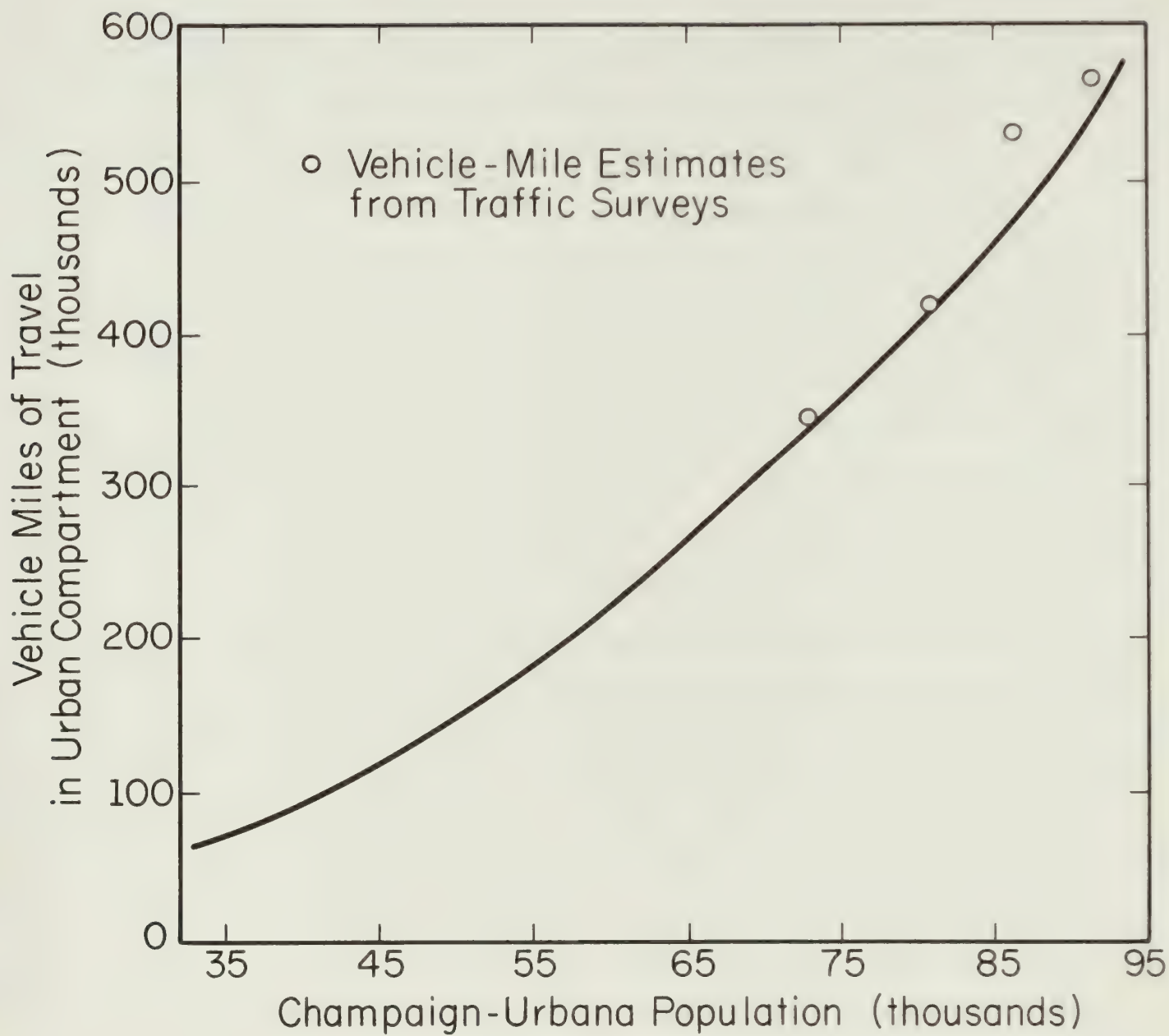


Figure 101

Travel Growth in Saline Branch Watershed Urban Compartment

### Data Analysis - Current Travel

Direct estimation of current traffic volumes on selected network links as determined by corridor land use activity and socioeconomic characteristics was a desirable output from the Traffic modeling study. This level of achievement, however, has not been attained by the modeling team. The direction of major urban transportation over the past fifteen years has been to obtain these link volumes indirectly through a four stage modeling sequence. These studies require massive data collection and analysis efforts and have been required since 1962 for all metropolitan areas over 50,000 population. Since the level of effort possible in the traffic modeling team was insufficient to develop a new, more direct modeling procedure for this project, the team coordinated its efforts with the traffic monitoring group to provide short run estimates of travel variation which could be used in the atmospheric modeling effort.

Vehicle miles of travel on the urban street classes defined by the traffic monitoring group (Ref. PR 3) were examined for a period of 15 years. The analysis was used to provide short-term annual growth estimates on major streets as well as monthly and daily travel variations for possible use in the atmospheric model.

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### C. Atmospheric Lead Transport Model

The lead content of the atmosphere is a key component of the ecosystem model. In the progress report for the period ending October, 1973 (PR3), a brief discussion of mathematical model predicting the lead content of air in the rural part of the ecosystem was given. In this report the model is completely developed and the computer simulation is given. A field sampling program for both rural and urban areas will also be described and the results compared to the model.

#### 1. Model of Atmospheric Transport of Lead Particulates

In this section, a mathematical model of the atmospheric transport of lead particulates in the ecosystem is described. By use of the model, and meteorological and lead emission data, an estimate can be made of the concentration of lead particulates and their rate of deposition.

Such information is of use both by itself and is input to the water, soil, plant, and animal modeling efforts. The section will begin with the general mathematical development of the equations governing the transport of lead particulates in the atmosphere. This section will discuss not only the mathematical development but also the restrictions inherent in such a model and



the rationale for this development in view of the available input data and field sampling available. Meteorological data available will next be discussed. This includes information on the wind speed and direction and the stability class. Daily averages for the rate of emission of lead particulates on the expressways and city streets are available as discussed elsewhere in this text. Since the meteorological parameters vary over the course of the day, it was necessary to estimate the temporal variation of the emission data over a 24-hour period. These data are fed to a computer program. The general logic of the program will be briefly discussed.

#### Mathematical Development

Dispersion of Particulates from a Point Source - Consider a point source of particulates of total strength  $Q$  g/sec. The emitted particulates have an arbitrary size distribution such that  $Q_k$  g/sec of a given particle size are emitted and the  $\sum Q_k = Q$ . If we assume that there is no coagulation or other interaction among the particles in the atmosphere, an assumption which is reasonable due to the low concentrations, then the dispersion of particles of a given particle size is independent of the transport of all other particles. The governing continuity equation for particles whose



size is denoted by index  $k$  is

$$\frac{\partial \rho_k}{\partial t} + \frac{\partial}{\partial x} (u \rho_k) + \frac{\partial}{\partial y} (v \rho_k) + \frac{\partial}{\partial z} (w \rho_k) = V_k \frac{\partial \rho_k}{\partial z} \quad (1)$$

where  $\rho_k$  is the particle concentration ( $\text{g/m}^3$ )  $x$ ,  $y$  and  $z$  are position in the direction of the wind, transverse to the wind, and in the vertical respectively and  $u$ ,  $v$ , and  $w$  are the components of the velocity in these three directions;  $t$  is time;  $V_k$  is the terminal settling velocity of particle  $k$ . Note that in Equation (1), it is assumed that there is no reaction or other interaction among the particles and that there is no volumetric source. Molecular diffusion is omitted. In addition, it is assumed that the velocity components  $u$ ,  $v$ , and  $w$  are known and that the particulates do not influence the meteorology. It is further assumed that the settling of the particles can be adequately representative by its terminal settling velocity. This assumption is commonly invoked (Cleary et al., 1973).

The velocity components and the lead particulate concentration are expanded into a time averaged and a fluctuating component where the time average part is noted by an overbar and a fluctuating component by a prime. These expansions are substituted into Equation (1) and

each term of the resulting equation is then time averaged. In addition,  $K_{kx}$ ,  $K_{ky}$ , and  $K_{kz}$ , the turbulent diffusion coefficients, are introduced, yielding

$$\begin{aligned} \frac{\partial \bar{\rho}_k}{\partial t} + \bar{u} \frac{\partial \bar{\rho}_k}{\partial x} + \bar{v} \frac{\partial \bar{\rho}_k}{\partial y} + \bar{w} \frac{\partial \bar{\rho}_k}{\partial z} = \frac{\partial}{\partial x} (K_{kx} \frac{\partial \bar{\rho}_k}{\partial x}) \\ + \frac{\partial}{\partial y} (K_{ky} \frac{\partial \bar{\rho}_k}{\partial y}) + \frac{\partial}{\partial z} (K_{kz} \frac{\partial \bar{\rho}_k}{\partial z}) + V_k \frac{\partial \bar{\rho}_k}{\partial z} \end{aligned} \quad (2)$$

Equation (2) is often used as a starting point in treating the movement of gaseous or particulate pollutants through the environment. Its derivation was briefly outlined here in order to point out the fact that it is an approximate equation valid under only certain restrictions (Lamb, 1973; Lamb and Seinfeld, 1973). In addition to the restrictions discussed above the spacial and temporal variations in pollutant concentrations must be larger than the respective scales of the atmospheric turbulence. Since the time scale in the atmosphere is of the order of a minute and the spacial scale the order of a kilometer, this restriction is clearly not met in the vicinity of a point source or a highway. Nevertheless, Equation (2) has been used successfully by several investigators with the values of the turbulent dispersion coefficients being obtained empirically (Crawford, 1973; Johnson et al., 1973; Johnstone et al., 1949; Sutton, 1947; Turner, 1970).

Equation (2) was solved assuming steady state conditions,  $\bar{u} = \text{a constant}$ ,  $\bar{v} = \bar{w} = 0$ ,  $K_{ky}$ ,  $K_{kz}$  are constant and that the dispersion in the direction of wind flow can be neglected with respect to convection.

With the above assumptions, the solution to Equation (2) is

$$\bar{\rho}_k = \frac{Q_k}{4\pi D_z^{1/2} K_y^{1/2} (x-x')} \exp \left[ \frac{-[(z-z')^2 + (y-y')^2] u}{4 K_z (x-x')} \right] \cdot \exp \left[ \frac{-V_k (z-z')}{2 K_z} \right] \cdot \exp \left[ \frac{-V_k^2 (x-x')}{4 K_z u} \right] \quad (3)$$

In solving Equation (2), it was assumed that a source of strength  $Q_k$  g/sec is emitted at position  $(x', y', z')$ . An estimate of the deposition rate of lead particulates to the ground ( $z = 0$ ) by both turbulent dispersion and gravitational settling can be obtained from Equation (3). Denoting the deposition rate to the ground by  $N_k$  (g/m<sup>2</sup> sec) there is

$$N_k = \frac{Q_k}{8\pi K_{kz}^{1/2} K_{ky}^{1/2} (x-x')} \left[ \frac{z' u}{(x-x')} + V_k \right] \cdot \exp \left[ \frac{-[z'^2 + (y-y')^2] u}{4 K_{kz} (x-x')} + \frac{V_k z'}{2 K_{kz}} - \frac{V_k^2 (x-x')}{4 u K_{kz}} \right] \quad (4)$$

Because of the approximation made in the boundary condition

at the air ground interface, the solution for the deposition rate to the ground given by Equation (4) is expected to be less accurate than the solution for the lead particulate concentration given by Equation (3).

Dispersion from a Line Source - The concentration and deposition rate to the ground of particulates emitted from a line source of arbitrary length and arbitrary angle to the wind (the wind always blows in the x direction) can be determined by integrating Equation (3) and (4). For example, consider a source of strength  $q_k$  (g/m sec) at height  $z'$  and on the line  $y' = mx' + c$  between the end points  $(x_1, y_1)$  and  $(x_2, y_2)$ . From Equation (3) the concentration at any point  $(x, y, z)$  is given by

$$\bar{\rho}_k = \frac{q_k}{2 u \pi} \frac{\sqrt{1 + m^2}}{m} \int_{y_1}^{y_2} \frac{1}{\sigma_y \sigma_z} \exp \left\{ \frac{-(z-z')^2}{2 \sigma_z^2} - \frac{(y-y')^2}{2 \sigma_y^2} - \frac{V_k (z-z')(x-x')}{u \sigma_z^2} - \frac{V_k^2 (x-x')^2}{2 u^2 \sigma_z^2} \right\} dy' \quad (5)$$

and the ground flux can be obtained from

$$N_k = \frac{q_k}{2 u \pi} \frac{\sqrt{1+m^2}}{m} \int_{y_1}^{y_2} \frac{1}{2} \left[ \frac{z'u}{x-x'} + V_k \right] \frac{1}{\sigma_z \sigma_y} \exp \left\{ \frac{-(z-z')^2}{2 \sigma_z^2} - \frac{(y-y')^2}{2 \sigma_y^2} - \frac{V_k (z-z')(x-x')}{u \sigma_z^2} - \frac{V_k^2 (x-x')^2}{2 u^2 \sigma_z^2} \right\} dy' \quad (6)$$

where  $\sigma_z = (2K_{kz} x/u)^{1/2}$  and  $\sigma_y = (2 K_{ky} x/u)^{1/2}$ .

As it will be seen below, it is sometimes useful to employ Equations (5) and (6) with the assumption that the distance  $x-x'$ , that is the distance from the source to the receptor, is constant along the highway. The integrals are replaced by exponential functions and error functions which reduces the computing time considerably. However, these formulas only hold exactly when the highway is perpendicular to the wind. When the highway is parallel to the wind,  $m$  is zero, and other limiting forms of Equations (5) and (6) can be found. When the highway is relatively long, the infinite line source formula can be used. The choice of which set of equations is to be used depends on the relative positions of the receptor and source.



### Applications of the Model to the Ecosystem

In applying the model to the ecosystem, particulate sources in and near the 140 square mile region are considered. Major highways are represented by a series of straight line segments and the urban area (Champaign-Urbana) is represented by 2 east-west and five major north-south streets. This highway and street network is shown in Figure 102. A computer program has been written from which the particle concentration and deposition rate can be found at any point in the ecosystem. Provision is made to include only those sources which make a significant contribution to the particle concentration at any given position. This numerical simulation is discussed below in further detail.

Wang and Rote (1973) have also used a finite line source model in predicting the dispersion of pollutants near O'Hare field in Chicago. However, a more common approach in predicting local pollutant patterns is that using area sources; for example, Randerson, 1970; Reynolds et al., 1973. Reynolds et al. have developed a model for gaseous pollutants in the Los Angeles airshed. A finite difference program with a distance between points of two miles was used to determine the transient behavior



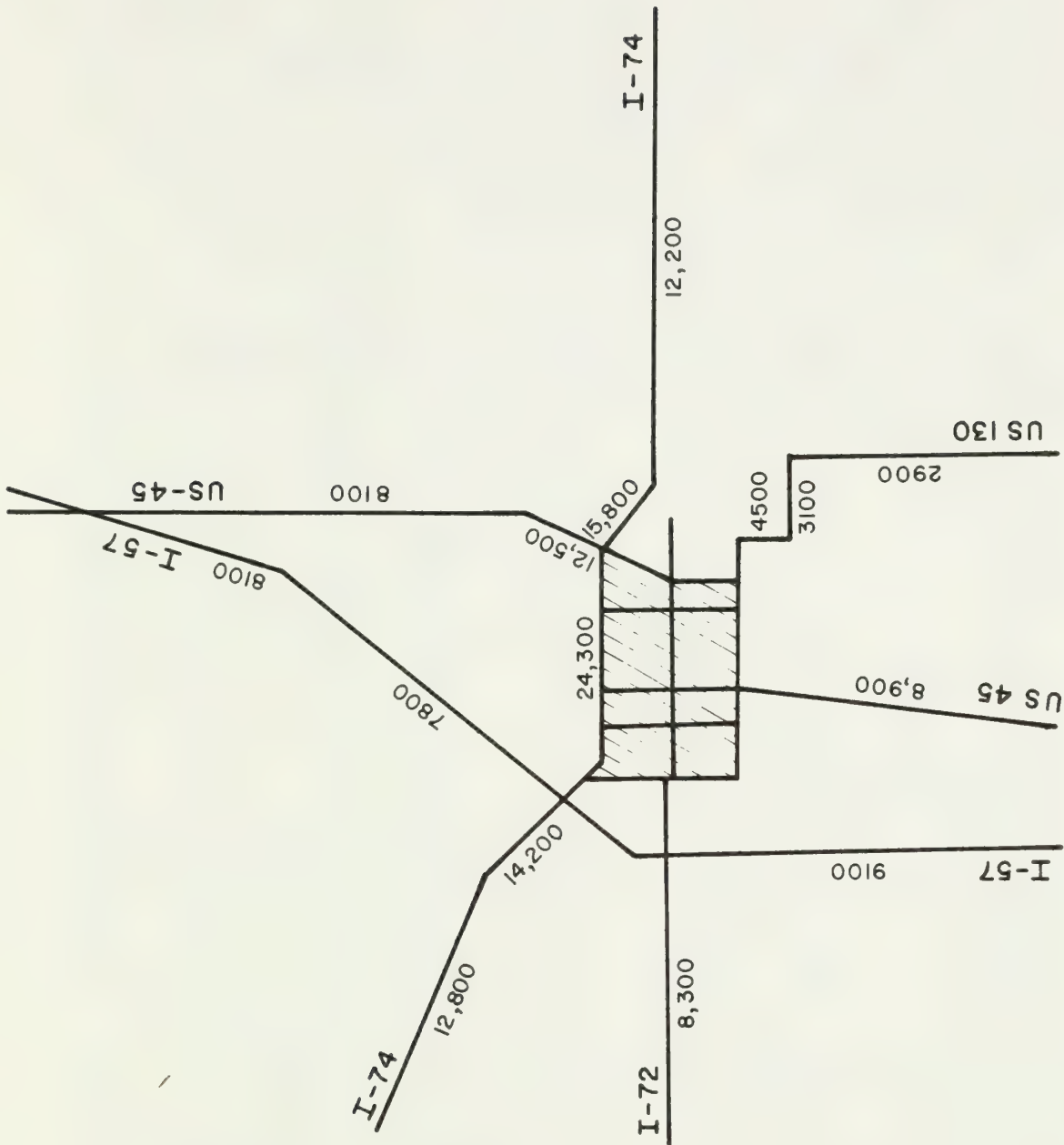


Figure 102  
Annual Daily Traffic Averages Major Roads in Champaign-  
Urbana Watershed Area

of the pollutants in this region. Such a method of solution is probably more applicable to a region such as Los Angeles where the pollutants in question are emitted more uniformly over the entire region. For the 140 square mile area of interest in the present study, the finite line source model is probably preferable, particularly in the rural areas where the sources of lead emission are widely separated. In addition, the modified Gaussian solutions are expected to be reasonably accurate for the length scales involved in the Illinois ecosystem and the assumption of a single, constant wind speed and direction for each hourly period is probably reasonable for the flat, open terrain of Champaign County.

#### Meteorological Data

Complete hourly weather data for the Champaign-Urbana area are available through the cooperation of the Flight Control Tower, Willard Airport, Savoy, Illinois. Data for October 3-4 are presented in Table 51 where hourly values for the prevailing wind speed, wind direction, cloud cover and ceiling are given. These data are assumed to be representative of the rural area of the ecosystem.

#### Emissions Data

Traffic in the watershed has been apportioned among 22 highways and streets shown for 1973 in Figure 102. Annual

Table 51  
Hourly Wind and Sky Condition Data  
Savoy, Illinois  
October, 1973

3					4				
Date	Wind	Wind		Cloud		Wind	Wind		Cloud
Hour	Direction	Speed	Ceiling	Cover	Hour	Direction	Speed	Ceiling	Cover
0050	09	6	40	3	0050	19	6	0	0
0150	09	5	60	6	0150	20	6	0	0
0250	09	5	60	6	0250	21	7	0	0
0350	09	5	60	6	0350	23	6	0	0
0450	26	5	60	6	0450	23	7	0	0
0530	26	15	80	10	0550	25	7	100	8
0550	26	10	80	10	0650	22	7	100	8
0625	19	10	150	10	0751	22	10	100	8
0650	18	5	150	10	0757	22	10	100	8
0750	17	4	150	10	0847	24	11	100	8
0850	11	8	150	10	0935	24	11	12	8
0950	12	12	100	8	0951	24	10	15	8
1050	17	6	250	10	1050	25	10	18	8
1150	19	14	120	10	1150	22	15	25	7
1250	19	12	250	10	1250	25	10	35	8
1350	19	10	250	10	1350	26	15	50	8
1450	19	5	250	10	1450	26	10	45	8
1550	16	7	200	8	1550	26	8	65	6
1650	15	6	200	10	1650	26	6	45	7
1750	15	5	120	10	1750	25	5	45	7
1850	7	5	120	10	1850	21	5	45	4
1954	12	8	100	10	1950	00	0	40	4
2050	14	12	100	10	2050	00	0	40	4
2150	16	8	100	10	2150	07	4	40	4
2250	22	7	100	10	2250	00	0	40	4
2350	22	8	100	10	2350	09	6	40	4

NOTES: Wind Direction: 00-36 in tens of degrees clockwise from true north, 00 = calm. For example, 18 = 180°, wind from south

Wind speed: in knots

Ceiling: in hundreds of feet, 0 is clear

Sky cover: in tenths, 0 = clear; 10 = totally overcast

daily traffic averages (vehicles/day) for the interstate highways and state roads have been obtained from Illinois Department of Transportation maps and from Professor E. Kannel, Civil Engineering Department, University of Illinois, Urbana. These are shown in Figure 102.

For the city, a figure for the daily total gasoline consumption on all streets of 36,300 gallons/day was obtained from Professor Kannel. When distributed equally among the seven city streets of the model a source strength for the city may be obtained (2.5 g lead/gallon gasoline is used in all computations). On city streets, 50% of the lead burned is emitted, while on interstates/state roads 70-80% is emitted. On interstates 15% of the traffic is attributed to diesel burning.

Traffic adjustment factors for the month of the year are shown in Table 52. Time distributions for traffic in the area are shown in Table 53.

Lead emission rates can be calculated and are shown in Table 54 under the following conditions:

1. Emission factors and monthly (October) adjustments applied to all roads. Truck factors applied only to interstates.
2. Gasoline consumptions were 15 miles per gallon on interstates, and 12.5 mpg in the city.

Table 52

## Traffic Adjustment Factors for Month of Year for Champaign-Urbana Area

Percent the Weekday Traffic is of the Annual Daily Average

<u>Road</u>	<u>Jan.</u>	<u>Feb.</u>	<u>Mar.</u>	<u>Apr.</u>	<u>May</u>	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.*</u>	<u>Oct.</u>	<u>Nov.</u>	<u>Dec.</u>
I-74	71	72	81	90	92	101	112	115	99/89	90	88	87
I-57	71	72	81	90	92	101	112	115	99/89	90	88	87
I-72	79	81	88	94	96	103	106	107	100/97	96	95	94
US 45	79	81	88	94	96	103	106	107	100/97	96	95	94
US 130	79	81	88	94	96	103	106	107	100/97	96	95	94
**City Streets	96	100	104	100	106	103	96	95	100	106	100	96

\* Sept. 1-15/16-30

\*\* Christmas, Easter, holidays, values approximately 20% less.

Table 53  
Temporal Traffic Distribution  
Champaign-Urbana Area  
Weekdays

<u>Time</u>	Percent of Annual Daily Traffic Average	
	<u>Urban Street</u>	<u>Rural Roads</u>
12 a.m.-0100	2.8%	2.3%
0100-0200	2.0	1.5
0200-0300	1.5	1.1
0300-0400	1.1	0.9
0400-0500	1.0	0.8
0500-0600	1.4	0.9
0600-0700	1.6	3.0
0700-0800	7.1	7.9
0800-0900	5.2	4.7
0900-1000	4.2	4.6
1000-1100	4.1	4.6
1100-1200	4.8	5.3
1200-1300	6.4	4.9
1300-1400	5.6	5.2
1400-1500	4.6	5.6
1500-1600	5.2	6.2
1600-1700	8.0	8.1
1700-1800	8.5	8.6
1800-1900	4.9	5.4
1900-2000	4.3	4.6
2000-2100	4.2	3.7
2100-2200	3.8	3.7
2200-2300	4.2	3.6
2300-2400	3.5	2.8



Table 54  
Lead Emission Strengths on Roads and Streets  
of Champaign-Urbana Watershed Model  
October, 1973

Map Coordinates				Road/Street	Uniform City* Lead Emission
<u>x<sub>1</sub></u>	<u>y<sub>1</sub></u>	<u>x<sub>2</sub></u>	<u>y<sub>2</sub></u>		
0.5	-5.0	0.5	3.0	I-57 South of City	$7.4 \times 10^{-6}$
0.5	3.0	5.8	9.5	I-57 South of City	$6.4 \times 10^{-6}$
5.8	9.5	8.8	18.8	I-57 North of City	$6.7 \times 10^{-6}$
7.5	2.6	1.7	2.6	I-74 East of City	$10.0 \times 10^{-6}$
7.5	2.6	6.3	3.6	I-74 East of City	$13.1 \times 10^{-6}$
6.3	3.6	2.3	3.6	I-74 East of City	$17.0 \times 10^{-6}$
2.3	3.6	0.2	5.8	I-74 East of City	$11.6 \times 10^{-6}$
0.2	5.8	-4.6	7.7	I-74 West of City	$10.5 \times 10^{-6}$
2.0	2.4	-5.0	2.4	I-72	$7.2 \times 10^{-6}$
5.75	2.2	5.75	1.0	Vine Street	$18.8 \times 10^{-6}$
5.0	1.0	5.0	3.6	Lincoln Avenue	$18.8 \times 10^{-6}$
3.75	1.0	3.75	3.6	Neil Street	$18.8 \times 10^{-6}$
3.0	1.0	3.0	3.6	Prospect Avenue	$18.8 \times 10^{-6}$
2.0	1.0	2.0	3.8	Mattis Avenue	$18.8 \times 10^{-6}$
2.0	1.0	6.5	1.0	Kirby/Florida Avenue	$18.8 \times 10^{-6}$
2.0	2.2	6.3	2.2	University Avenue	$18.8 \times 10^{-6}$
7.0	5.0	7.0	16.0	US 45 North	$8.4 \times 10^{-6}$
7.0	5.0	5.75	2.2	US 45 North	$12.5 \times 10^{-6}$
3.7	1.0	2.8	-5.0	US 45 South	$9.2 \times 10^{-6}$
6.5	1.0	6.5	0.0	US 130 North	$4.1 \times 10^{-6}$
6.5	0.0	8.0	0.0	US 130 North	$2.8 \times 10^{-6}$
8.0	0.0	8.0	-5.0	US 130 South	$3.0 \times 10^{-6}$

\* g/m-s

Tables 53, 54 together give a complete traffic picture for the area.

The size distribution of the lead particulates as used in the present modeling study was as follows: three size ranges of particulates having median diameters of 1.0, 10.0, and 20.0  $\mu\text{m}$  were used and the percent of total lead in each of the three size ranges was 75%, 10% and 15% respectively. This size distribution is consistent with the data of Hirschler et al., (1957) and Mueller et al., (1964). Recent studies by Habibi (1973) based on slightly different measurement techniques (Habibi, 1970) indicates a definite shift toward the heavy particulate size range. The effect of this on the model is being investigated.

#### Numerical Simulation

With all the information on meteorology, highways and emission as the input data, the simulation program would generate a grand-level concentration and flux map covering the entire area of interest. Then isopleths can be determined and compared to the field experimental results.

Since considerable amount of computation is involved in generating the maps, the proper formula must be selected to minimize the computing time; also, each approximation formula had a limited range of applicability. It was obvious that an extensive geometrical test was needed

to incorporate all the formulas to form a useful algorithmic scheme.

Before the test, the coordinate of the highway was transformed to a new coordinate system which the receptor was the origin and the direction of wind was the positive  $x$  direction. If the highway is located entirely downwind of the receptor, it definitely had no contribution. Because of turbulent dispersion, particles emitted from a source spread horizontally, and the amount of spread is determined by the quantity  $\sigma_y$ . At a transverse distance greater than  $3 \sigma_y$  from a point directly downwind from a source, the particulate concentration is less than one percent of its centerline value. Thus, if a receptor is greater than  $3 \sigma_y$  from the centerline, the contribution from that source is neglected; thus, only part of some highways may contribute to a given receptor. The  $3 \sigma_y$  criterion was also used to define the infinite line source so that limiting forms of Equations (5) and (6) could be used.

When the slope of a highway was small, (relative to the wind direction) the small angle approximations are preferable since less computing time was required, besides the accuracies of Equations (5) and (6) are poor under

these conditions due to the limited precision on the evaluating of error functions. The use of these small angle formulas were limited for the slope less than 0.05 and satisfactory results were obtained.

In using those formulas for which the assumption was made that the downwind distance  $x-x'$  is constant, the straight line sources were broken up into several sections in order to improve the accuracy of the computation.

The computer program can thus calculate the particulate concentration and deposition rate to the ground given the emissions from all streets and highways, the wind direction and speed, and the stability class.

The dispersion coefficients  $\sigma_y$ ,  $\sigma_z$  depend on downwind distance and on the particular stability state of the atmosphere. The methods of Turner, 1961 and 1970 were used. There are six possible stability classes ranging from highly unstable through neutral to highly stable. The stability class depends on the wind speed and incident solar radiation (determined by cloud cover, ceiling and solar angle). An average stability class was determined for each hour of the day. As noted above the estimation of the deposition rate is not as accurate as that of the particulate concentration. 24-hour averages

at a network of receptor points are determined in the following manner. Meteorological and emissions data are available on an hourly basis as noted above. The 24-hour average is found by summing all hourly contributions. Before discussing the results of the model simulation, the field sampling program must be described.

## 2. Field Sampling Methodology

The field sampling program encompassed two types of experimental investigations. One study focused on measuring the distribution of ambient lead levels, particle size distribution, and deposition rates in the rural section of a 140 square-mile ecosystem while the other study examined these variables in the urban environment. Each of these studies will be discussed separately.

### Rural Study

The Illinois rural study utilized eight General Metals Works high volume samplers for making field measurements. In order to utilize these field instruments in the most effective way, an analytical model was used for locating the samplers. From the concentration distributions predicted by the model, the high volume samplers were placed to most effectively test the model. The location of the samplers is given in Figure 5, page 16.



The high volume samplers were powered by electrical outlets utilizing either existing power outlets in the field or propane fueled electrical generators. Pictures of both types of test site are given in Figure 103. Gelman 8"x10", GA-1 Metrical triacetate filters (5  $\mu$  pore size) were initially used as primary filters with standard 8"x10", type A, fiberglass filters (.8  $\mu$  pore size) used for back-up secondary filters. Both filters were analyzed for lead content. The analytical procedures for determining the lead content of the filter involved cutting the filter into 8 parts and analysis of 3 random cuttings. Standard University of Illinois (Urbana) procedures of dry ashing (temperature programmed to 450°C), HCl digestion and atomic absorption spectrometry were used. It was found that utilizing a single 8"x10" fiberglass filter gave equivalent results to those obtained using the dual filter arrangement and the single filter was used in subsequent tests.

Calibration of the high volume blowers was accomplished through the use of a General Metal Works calibration kit and manometer. Both the calibration kit and procedure used were standard as specified in Section 8.1 of Vol. 36, No. 21, (Saturday, January 30, 1971) of the Federal Register and the blower operation manual with a slight modification.



Figure 103  
Typical Test Sites



This modification involved the substitution of a manometer for the rotameter at the blower exit orifice. During the course of the experimental program, 24-hour runs were normally undertaken.

High volume sampler runs were made using an Anderson particle sizing head at selected locations. This special head is designed to classify atmospheric particulates by aerodynamic size into the following equivalent ranges: 7 microns and above, 3.3 to 7 microns, 2.0 to 3.3 microns, 1.1 to 2.0 microns, and 0.01 to 1.1 microns.

The flux of lead particulates was measured using a modified dust fall station. A polyethylene canister, 6 inches in diameter, and 9 inches deep, was mounted 3 feet off the ground. Additional canisters were placed in the ground so that the canister lip was three inches off the ground. The canister was filled with an isopropyl alcohol solution with a known lead blank. The level in the canister was maintained constant at a depth of 1 inch. Deposition measurements were made over a period of 30 days. Each canister was fitted with a tight fitting lid to ensure no loss of fluid during transportation.

#### Urban Study

A study to determine the ambient lead particulate concentration and deposition levels in the community of

Champaign-Urbana, Illinois, has recently been undertaken. To date, four sampling stations are in operation. Two stations are located in a suburban section of the community (Stations D and H on Figure 102), while the remaining two stations are located near the center of the University of Illinois at Urbana campus, at the Roger Adams Laboratory Building (Station K, Figure 102). One campus station is located in front of the laboratory, while the other is on the roof of the four-story building. Total lead particulates, particle size distribution and deposition measurements are being made at all four stations. The sampling techniques for each of these measurements are the same as for the rural area discussed earlier.

### 3. Results

Total atmospheric lead concentrations in the rural and suburban area were measured over a 6-month period but the later (August, 1973 - February, 1974) samples have not been analyzed as yet. Data are presently available for 24-hour periods on twenty days, 3 in August, 2 in September, 7 in October, 6 in November and 2 in December. Daily measurements taken on October 3-4 are shown in Table 55. The data spread between rural sites is small and this is reflected in the overall means for each site for the twenty days as

Table 55  
Total Lead Concentrations  
October 3-4, 1973

<u>Station</u>	<u>Measured</u>	<u>Predicted*</u>
A	.295	.049
B	.331	.043
C	.279	.024
Rural E	.131	.012
F	.181	.027
G	.328	.078
I	.279	.034
J	.241	.031
Suburban D	.511	Model Not Applicable
H	.434	Model Not Applicable
Urban K, roof	.545	Model Not Applicable
K, ground	.648	Model Not Applicable

\*Without Background



shown in Table 56 The overall rural mean is  $.23 \mu\text{g}/\text{m}^3$  while the overall suburban mean is  $.36 \mu\text{g}/\text{m}^3$ .

From Table 56 it is seen that the most remote stations, E and I, have somewhat lower means than those closest to the urban area--such as stations G and A.

A two-way analysis of variance has been carried out on the rural data. The problem is rather complex because some measurements were not made on specific days at specific sites due to equipment malfunction. Computer analysis of the problem indicates that at the 95% confidence level (F-test method) some of the means shown in Table 56 are statistically different. It would appear from Table 56 that at least the site E mean is significantly different from some of the other means.

Replicate sampling carried out in the urban area give a surprisingly high precision--approximately 10%. However, it is felt a more realistic value is 25% for the field sampling program.

The statistical analysis also indicated that day to day variation in lead concentration at a given site was greater than the site to site variation on a given day. This is seen from Figure 104, the October lead concentration for sites A and B.

Table 56  
Mean Lead Concentrations

<u>Five Months/Site</u>	<u>Measured Range</u>	<u>Measured Mean</u>	<u>Predicted Mean</u>
A	.17-.52	.28	.25
B	.03-.58	.28	.24
Rural C	.03-.44	.24	.24
E	.07-.42	.19	.22
F	.06-.44	.25	.25
G	.09-.47	.27	.27
I	.06-.3	.22	.23
J	.04-.58	.24	.24
Suburban D	.09-1.04	.35	Model Not Applicable
H	.09-.68	.36	Model Not Applicable
Three Months			
Urban K, roof	.1-.85	.45	Model Not Applicable
K, ground	.09-1.06	.54	Model Not Applicable



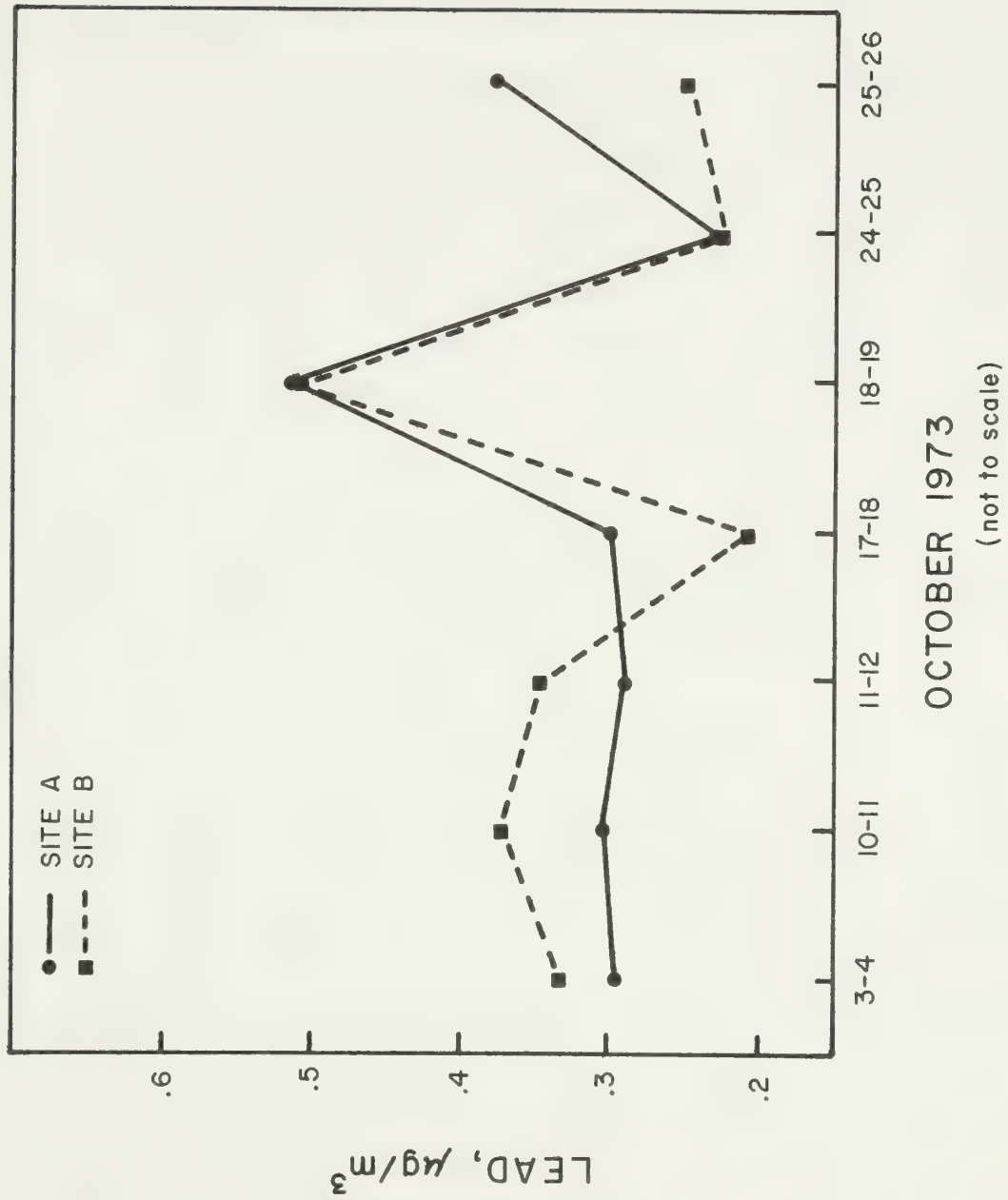


Figure 104  
Lead Concentration Variation in October, 1973, Sites A and B

Results from the computer simulations (an example is shown in Table 56) indicates that background lead content in the rural area must be taken into account. This has not been done in the model described in the first section of this chapter. The background may be estimated in the following manner. Stations E and I are the most remote field sites. The background lead concentration may be taken as the average of those values measured at E and I on those days when the model predicts very low lead concentrations ( $\leq .01 \mu\text{g}/\text{m}^3$ ). The background value is found to be  $.20 \mu\text{g}/\text{m}^3$ .

Alternately, a statistical model follows: Let  $y_{ij}$  = measured lead concentration at site  $i$  on day  $j$ , and  $x_{ij}$  be the predicted value. Then

$$y_{ij} = x_{ij} + \mu + e_{ij} \quad (7)$$

where  $\mu$  = background and  $e_{ij}$  is an error term. In this model,  $\mu$  may be taken as the mean of  $z_{ij} = y_{ij} - x_{ij}$ . For the five-month period,  $\mu$  is  $.23 \mu\text{g}/\text{m}^3$ . Both methods yield similar results. There are various methods available to check the "reasonableness" of Equation (7).

It has been found by the Kolmogorov-Smyrnov test that all the values of  $z_{ij}$  come from the same distribution

(Lindgren, 1963). Further work is in progress. Using a background value of  $.215 \mu\text{g}/\text{m}^3$ , the predicted values of the total lead concentration in air at the rural sites is shown in Table 56.

The predicted and measured values agree fairly well. It is seen that although Champaign-Urbana makes some contribution to the total lead concentration in the rural air, most of the lead comes from other sources.

Measurements were made in the urban area beginning in October, 1973 and data are shown in Tables 55 and 56. For October, the rural average was  $.29 \mu\text{g}/\text{m}^3$ . For November the rural average was  $.19 \mu\text{g}/\text{m}^3$  while the urban average was  $.4 \mu\text{g}/\text{m}^3$ . Thus about a factor of two difference the city and rural areas.

Some data were obtained on the variation of total lead concentration with height in the urban area. As shown in Tables 55 and 56, the variation is slight.

Preliminary particle size data indicate that lead occurs in the smaller particulate sizes. In the rural-suburban area approximately 80% is collected on the back-up filter to the Andersen sampler indicating an aerodynamic size range,  $.01$ - $1.1 \mu$ . For the urban area approximately 70% lies in this range. This agrees with the data of Lee et al., 1972.

No data have been received from the dustfall study as yet.

#### Summary

In summary then, a mathematical model which can predict rural air lead concentrations has been developed. The rural air lead concentration is relatively uniform with a mean value of  $.23 \mu\text{g}/\text{m}^3$ . Mean lead concentrations in the suburban area were  $.36 \mu\text{g}/\text{m}^3$  while preliminary urban data gave a mean of  $.54 \mu\text{g}/\text{m}^3$ . Lead particulates are concentrated in the  $<1 \mu$  size range and air lead concentrations show only slight variation with height.

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#### D. Hydrologic Transport Model

A linear, first-order differential equation model has been adopted, with several modifications, as the initial model of lead movement by surface water due to a rainfall-runoff event in an urban area. The model is described in terms of a dependence of the amount of lead remaining on the amount of lead originally present and on the quantity of water discharged from the region.

The model is based on a theoretical model of constituent discharge from a completely mixed, constant volume tank. In such a tank, the lead concentration can be represented to

$$c = \frac{P}{v}$$

where:

c represents the concentration (of lead in mass/volume) in the tank

P represents the mass of lead present and

v represents the volume of the tank

Then, with the completely mixed assumption, an equation for the incremental discharge of lead from the tank can be written

$$\frac{dP}{dt} = -C q(t)$$

or

$$\frac{dP}{P} = -\frac{1}{V} q(t) dt$$

or

$$\frac{dP}{P} = -\frac{1}{V} q(t) dt$$

The model considers only the total mass of lead discharged during a complete rainfall-runoff event. Since such an event occurs within a relatively short time in an urban terrestrial ecosystem, since instantaneous lead concentrations in storm runoff are not particularly important in themselves, and since the principal interest in the model is its use in a longer, time-based mass balance accounting, the interest in only the total mass of lead discharged is well justified. Thus, the desire is to use the model in describing the mass of lead removed from a given region within surface water flow due to an event. The independent variables in the relationship are the mass of lead present at the beginning of the event and the total quantity of water discharged during the event. The single parameter  $\left(\frac{1}{V}\right)$  would characterize the particular area of concern.

In the case of the particular urban region to which this model is being applied, a third modification is necessary. The watershed of interest is that of Boneyard Creek

in Champaign-Urbana, Illinois. It consists of the 3.58 square miles of intensively urban area above USGS Stream Gage No. 3-3370 which is located on the campus of the University of Illinois. This particular watershed has been the subject of intensive hydrologic studies by the Illinois State Water Survey and it has been found by Terstriep and Stall (1969) that essentially the only contribution from rainfall to storm runoff comes from the directly connected impervious areas of the basin, that is, from streets, parking lots, roofs, and so forth which are directly served by the storm sewer system. They have suggested that these directly connected impervious surfaces constitute 22% of the basin area and have published the rainfall and runoff data for 28 storms. The regression equation for these data is

$$Q_b = -0.016 + 0.22r$$

where:

$Q_b$  represents the total storm runoff in inches spread over a 3.58 square mile area and

$r$  represents the total event rainfall in inches

This empirical equation, is precisely that which would be produced theoretically by suggesting that only the directly connected impervious areas contribute, that they require

0.073 inches of rainfall for initial wetting of these surfaces, and that the areas of interest do constitute 22% of the basin surface.

If no runoff occurs from either the previous areas of the basin or the nondirectly connected impervious areas, it is unreasonable to suggest that those areas could contribute lead to the lead discharge in stormwater. Thus, the region of interest in applying the lead transport submodel must be defined to include only the directly connected impervious surfaces of the basin. On that basis the model is:

$$\Delta P = P_a - P_b = P_a \left(1 - e^{-\frac{t}{v} Q_b}\right)$$

where:

$P_a$  represents the mass of lead present on the directly connected impervious areas at time  $a$ , the start of the rainfall event

$P_b$  represents the mass present at time  $b$ , the end of the event

$Q_b$  represents the total surface water runoff from the directly connected impervious areas and from the basin as a whole due to the event,

$v$  represents the directly connected impervious

area's "volume" in the analogy with a completely mixed tank, and

$\Delta P$  represents the total mass of lead discharged from the directly connected impervious areas and from the basin as a whole due to the event.

At present there is not sufficient data on the lead mass of storm water runoff to adequately evaluate the model parameters. A proper calibration would require estimates of lead mass on the connected impervious area, water discharge, and lead concentration in the storm runoff water from several storms. These data should be available by September, 1974.

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### E. Distribution of Lead in Rats Model

The following model was developed to study the dynamics of lead in rats. The model is based on two experiments by Forbes (see PR3, pg. 179 and pg. 316).

The model parameters were first estimated in adult rats receiving 160ppm lead nitrate for 8 weeks and a lead free diet for an additional 8 weeks. A group of juvenile rats fed 150ppm lead nitrate for time schedule. The model was modified by adding a growth term to improve the model fit.

The model as presented can be used to study either mass or concentration of lead in adult or juvenile animals. The model contains several compartments shown in Figure 105. Conceptually the model can be other organs, mammals or metals with appropriate change in parameter values.

The main assumptions of the model are:

- a) the transfer of the contaminant, namely lead, within the body is accomplished via the blood.
- b) the uptake and elimination of the contaminant by a compartment follow a first order law. This assumption implies that the instantaneous transfer rate from any given organ is directly proportional to the amount present in that organ.

- c) the transfer coefficients are assumed to be constants.
- d) each organ represented by a compartment is assumed homogenous and uniform, and organ growth follows a logistic curve.
- e) mass equilibrium is satisfied at any given organ and for the body as a whole.

In this particular model, only lead ingested with food is considered. Other possible modes are neglected. Also, only outputs via the urine, and feces are considered. The function of an organ is considered as being separated from its physical entity. Thus, the concentration of lead in the urine is assumed here to be proportional to the concentration of lead in the tissue of the kidney. Other interpretations could be used.

The mathematical model describing the uptake and elimination of lead by adult rats as derived from Figure 105 is given by a set of first order linear differential equations with constant parameters. Each equation states that the rate of change in accumulation within a given organ is equal to the uptake rate minus the elimination rate.

The input rates to the system are:

$$R_{fd} = \sum_{n=1}^n IR_n \cdot CE_n \cdot X_n \quad (8)$$

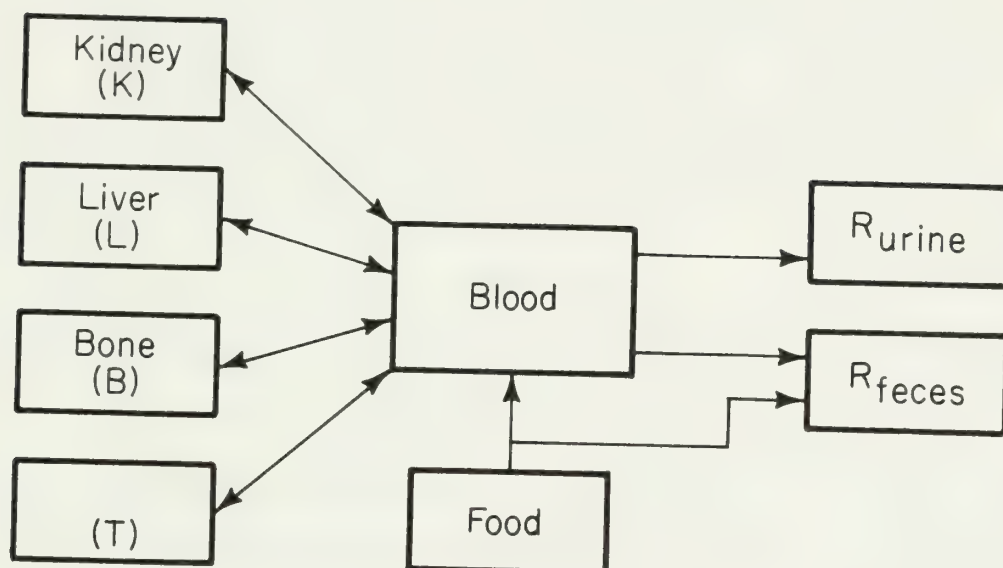


Figure 105

Box Diagram of Compartments and Flow Pathways of Lead in Rats.

The output rates from the system are given as:

$$FE = \alpha_f' \cdot BL + \sum_{n=1}^n IR_n \cdot CE_n \cdot (1-X_n) \quad (9)$$

$$UR = \alpha' \cdot (BL) \quad (10)$$

$$\dot{K} = -\alpha_K \cdot K + \alpha_K' \cdot BL \quad (11)$$

$$\dot{L} = -\alpha_L \cdot L + \alpha_L' \cdot BL \quad (12)$$

$$\dot{B} = -\alpha_B \cdot B + \alpha_B' \cdot BL \quad (13)$$

$$\dot{T} = -\alpha_T \cdot T + \alpha_T' \cdot BL \quad (14)$$

$$\dot{BL} = -\dot{K} - \dot{L} - \dot{B} - \dot{T} + R_{fd} - \alpha_u' \cdot BL - \alpha_f' \cdot BL \quad (15)$$

Where:

K, L, B, BL represent the amount of lead respectively in the Kidney, Liver, Bone, and Blood.

T represents the amount of lead in all other tissues, organs, and sinks not included in the model. The inclusion of this conceptual organ allows the conservation of equilibrium in the whole system.

UR, FE represents the amount of lead respectively in the urine and feces.

$\alpha_i$  represent the rate constant for the transfer of lead from organ i to the blood.

$\dot{K}$ ,  $\dot{L}$ ,  $\dot{B}$ ,  $\dot{BL}$ ,  $\dot{T}$  are the time derivatives of the respective compartments.

$\alpha'_i$  represent the rate constant for the transfer of lead from the blood to organ i.

$\alpha'_u, \alpha'_f$  represent respectively, the rate constant for the transfer of lead from the blood to the urine and feces.

$R_{fd}'$  represent the rate input of lead to the blood from food.

$IR_n$  represent the ingestion rate of food type n.

$CE_n$  represent the concentration of lead in food type n.

$X_n$  represent the fraction of lead absorbed into the blood from food type n.

The model was initially fitted to the adult animals receiving 160 ppm lead nitrate using a CSMP integrating package on an IBM 360/75. The model results are shown in Figure 106, solid lines and points, the transfer coefficients are listed in Table 57. As shown in Figure 106 the model gives a reasonable fit for adult rats. The blood corresponds to a rapid exchange pool, the liver and the kidney are immediate pools, and the bone is a slow exchange pool. The release period, week 8 to 16, was not long enough to clearly identify an irreversible pool. The (approximate) half times of lead in the blood, kidney, liver and bone are respectively: .5, 1, 1, and 8 weeks.

The model was then tested against the juvenile animals,

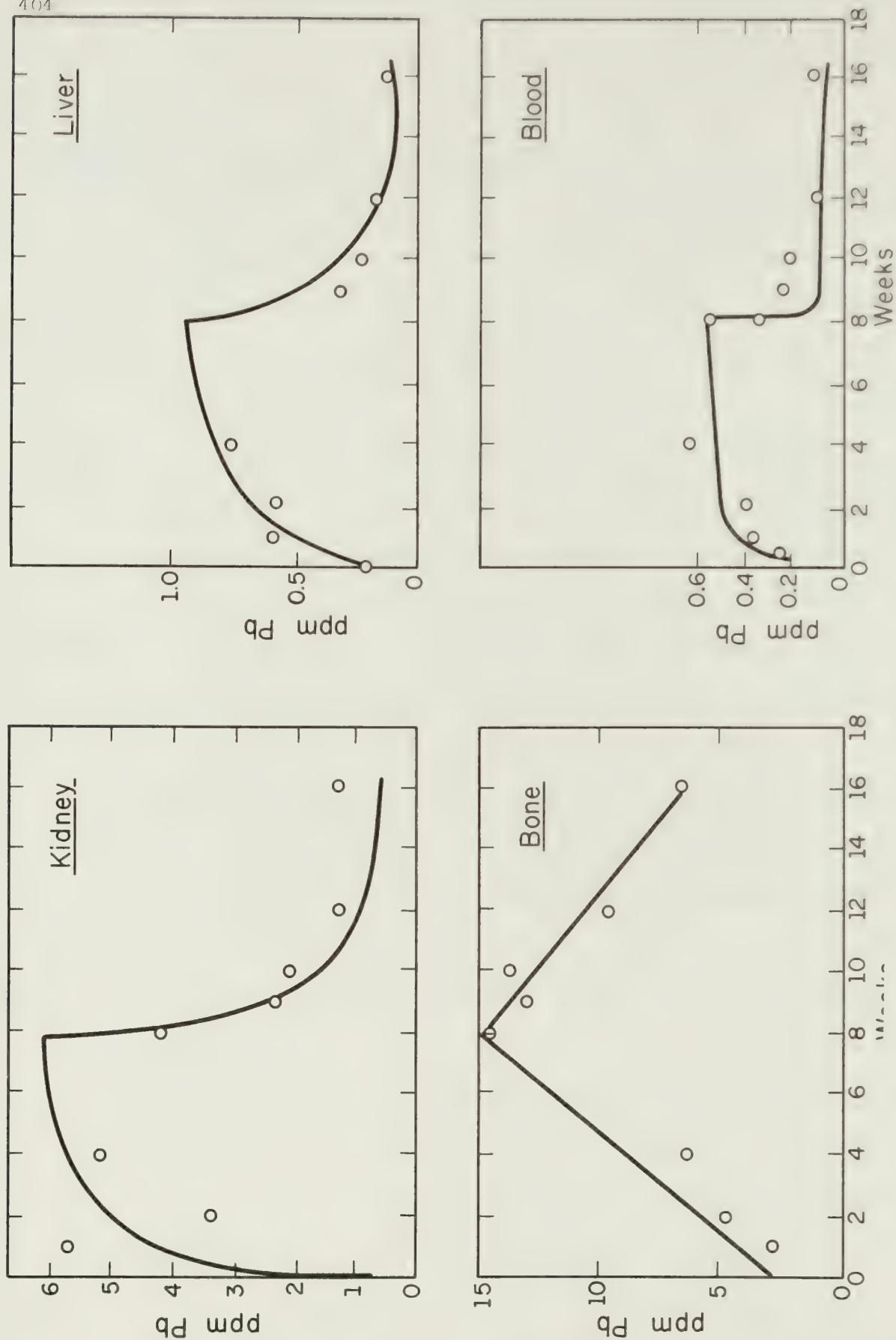


Figure 100  
Lead Uptake by Organs for Adult Rat



Table 57  
Model Parameter Values

Compartment	Uptake		Release	Growth Function	
	Mature Tissue	New Tissue		A	K
Kidney	.9	14.0	1.3	2.7	.5
Liver	.5	.7	0.9	15.2	.09
Bone	4.0	10.0	.12	30.	.04
Blood	.045	.045	40.	50.	.01

Figure solid line, and it is evident that the model is inadequate for young animals. An examination of the data on young rats show that:

- 1) The uptake and accumulation of lead for growing rats, is higher than for adult rats at a given input.
- 2) The additional lead uptake accrued mostly during the growing period.

These observations suggest that a new factor in the model should be added to account for growth. A simple formulation is prepared based on the rate of growth of a given organ.

Let  $\frac{dW_i}{dt}$  = rate of change of the weight of organ i

then, the additional uptake of lead generated by growth can be approximated by

$$\lambda * i \cdot \frac{dW_i}{dT} \cdot (BL) \quad (17)$$

where

$K*i$  = growth transfer coefficient for organ i

$W_i$  = weight of organ i at time t

$BL$  = as defined previously, i.e., lead concentration in the blood at time t.

The expression given in (17) was added to the model for each organ as given by equ. (12) to equ. (16). The blood

compartment was kept the same. Thus for example, equ. (12) becomes

$$\frac{d(k)}{dt} = \alpha_k \cdot (K) + \alpha'_k \cdot (bl) + \alpha_k^* \frac{I}{k} + \frac{d(W)}{dt} \cdot (bl)$$

the data on organ weights were fitted to a logistic curve of the type

$$\frac{dW}{dt} = K \cdot W(A-W)$$

where

$K$  = constant

$A$  = adult weight of organ

The resulting model is a nonlinear compartmental model. The nonlinear portion of the model disappears after the growing period is terminated. The same coefficients determined previously were used and the  $\alpha_i$  were determined by fitting the new model to the data available.

The results of the additional term can be seen in Figure 107 dashed line and open circles. The model as modified gives a better fit and bone compartments which have higher concentrations of lead than the blood or liver. The model also gives a better fit for the liver. The initial spikes for the liver and kidney are caused by the growing tissue. After these two organs cease to grow, about the fourth week, the concentrations decrease to that

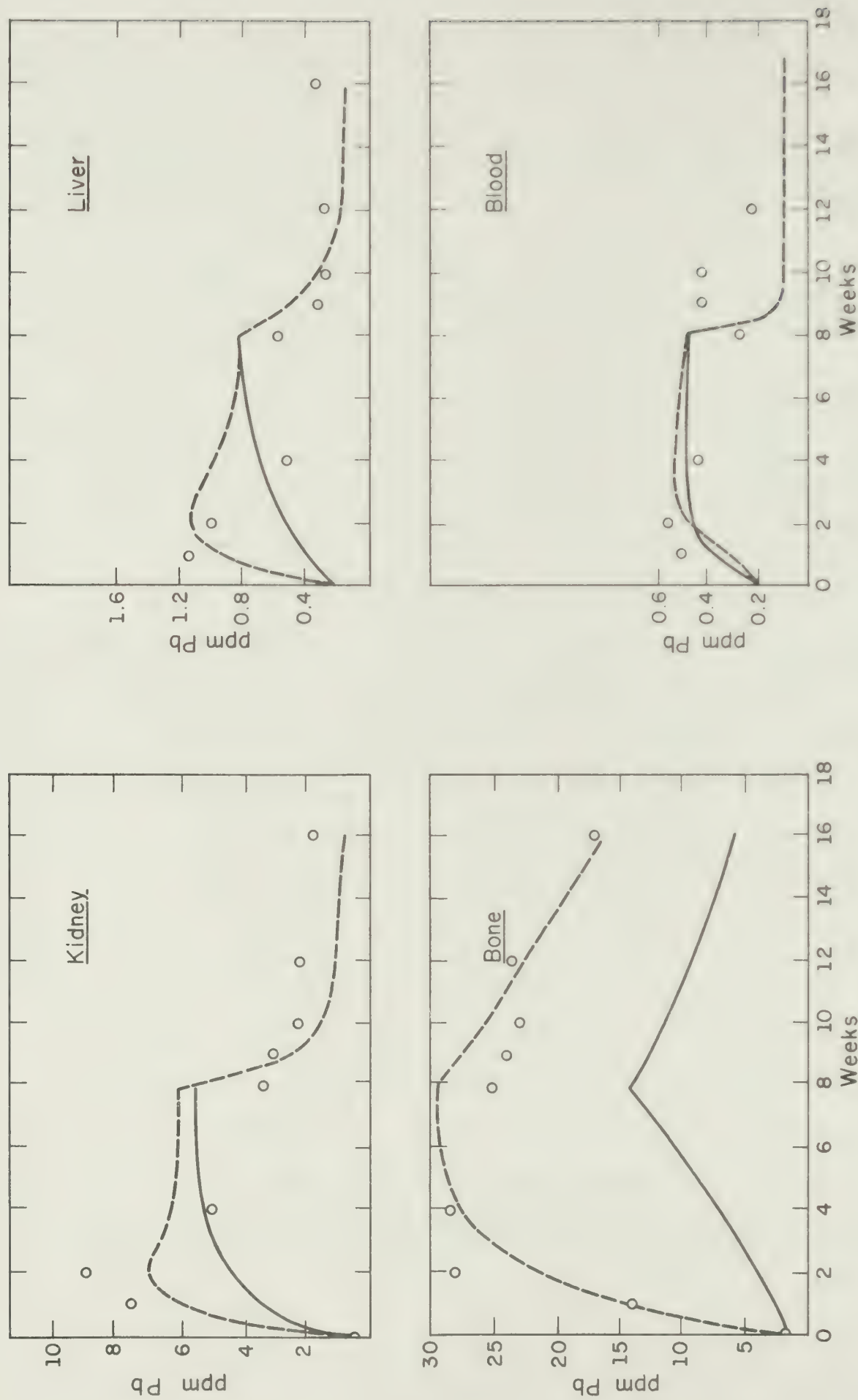


Figure 107

predicted for adult animals. The bone reaches a high level and slowly falls after the animals are placed on a "lead free diet". This is indicative of slow release from the bone and is in agreement with existing hypotheses concerning the bone as a long term sink for lead.

A comparison of the uptake rates of growing versus mature tissue may in part explain the increased sensitivity of young animals to lead. The uptake rate of new bone tissue is 2.5 times that of mature tissue, and kidney is 70 times that of the mature tissue. The new tissue for the liver has only a slightly higher uptake rate than the mature tissue. The very high uptake rate of the kidney indicates that critical levels in this organ could be reached if very young animals were used.

When the model was tested relative to different input levels, such as 320 ppm and 40 ppm of lead, the deviations were higher. This observation may suggest that the transfer coefficients are not constant and may depend on the level of input. This hypothesis may be acceptable if at high input level of lead, biological damage occurred that could impair normal biological behavior. No evidence of this was found in the rats. The accumulation of lead in certain organs did not reflect the level of input that was fed to

the rats. Another explanation is that the animals receiving lead in their diet consumed less feed thereby having a lower ingestion rate of lead. Additional information is needed to make this distinction.



VI. SOCIAL SCIENCES

G. Provenzano

## VI. Cost-Benefit Implications of Federal Regulations for Removing Lead Additives From Gasoline

The research that is reported in the following sections examines some of the cost-benefit implications of the recently implemented federal regulations for controlling the use of lead additives in gasoline. This research is preliminary to undertaking a complete cost-benefit analysis of removing lead from gasoline. A complete cost-benefit analysis is being proposed as part of the final phase of the University of Illinois study of environmental pollution by lead.

Section A below outlines some of the costs that are associated with the removal of lead additives from gasoline. These costs will result primarily from increases in the consumption of energy resources.

More energy will be required (1) to produce unleaded gasoline and (2) to satisfy the fuel demands of increasing numbers of cars that can run on lower-octane unleaded gasoline. A careful evaluation of the energy implications of various strategies for lead removal is clearly warranted in view of the recent concern over shortages of energy supplies.

Section B defines a methodology-risk-benefit analysis for assessing in economic terms the benefits associated with removing lead from gasoline. These benefits include a

reduction in the risks of adverse physiological effects of automotive emissions of lead on human health, animals, and crops. No effort has been made to quantify the benefits of removing lead from gasoline.

Section A. The Energy, Economic and Technological Impacts  
of Regulations for Removing Lead Additives from Gasoline

Under the provisions of the Clean Air Act of 1970, the U.S. Environmental Protection Agency has promulgated two sets of restrictions on the use of lead additives in gasoline. EPA has ordered major gasoline retailers to sell one grade of unleaded gasoline beginning July 1, 1974 (Federal Register, 1973a). In addition the Agency has implemented a five year phased-reduction schedule for reducing the maximum allowable lead content of regular and premium grades of gasoline (Federal Register, 1973c). Both of these regulations are part of EPA's overall strategy for eliminating automobile air pollution.

The general availability of unleaded gasoline will enable automobile manufacturers to install catalytic emissions control devices on 1975 model cars. Detroit has developed the catalytic system as a means of complying with the tough 1975-76 federal automotive emissions standards. For 1975 cars the catalytic controls have been designed to convert emissions of carbon monoxide and unburned hydrocarbons into harmless carbon dioxide and water vapor. Catalytic converters may also be used on 1976 cars to control nitrogen dioxide emissions. In either case, however, the effectiveness of catalytic devices in reducing automotive pollutants will be

severely limited if the combustion products of lead additives are also present in the exhaust.

Lead in gasoline is also the major source of lead that is emitted into the atmosphere, and the phased reduction schedule has been designed to reduce the health hazards of automotive lead emissions by removing lead from gasoline. Airborne lead can be directly inhaled and adsorbed into the body through the lungs, or lead can settle out of the air and contaminate soil where it becomes a potential source of ingestible lead for children. Because of the toxic properties of lead, EPA has concluded that the continued discharge of automotive lead emissions into the environment presents a public health hazard. The Agency has found it necessary to reduce lead emissions by reducing the amount of lead in all grades of gasoline.

The full implementation of both EPA regulations will significantly reduce the widespread use and, hence, the energy and cost saving benefits of lead additives in gasoline. Adding tetraethyl lead and other lead antiknock agents to gasoline has provided a dual means of holding down the total energy requirements for automobile transportation. On the one hand, the use of lead additives has enabled petroleum refiners to conserve energy resources

during the production of high octane fuels. On the other, the availability of high octane gasoline has permitted continued improvements in automotive engine fuel economy.

The petroleum industry has used tetraethyl lead since the 1920's as a low-cost means of increasing gasoline octane ratings. The addition of a few grams of lead to each gallon of gasoline enables refiners to cut down on processing requirements and to obtain more gasoline per barrel of crude oil. For these reasons unleaded or low-lead, high octane gasolines are more costly to produce than the present leaded grades.

High octane gasolines are essential for the satisfactory operation of high compression engines. Over the past decades the automobile industry has steadily improved engine fuel economy by increasing compression ratios. In 1970 the auto makers reversed this trend and decreased compression ratios to accomodate the use of lead sensitive emissions control devices (in 1975) and lower octane unleaded gasoline. This change has had an adverse effect on energy consumption by automobiles.

Because of the importance of these economic and energy-saving benefits, EPA's demands have generated many questions concerning the economic and technical prudence of an emissions



control strategy that demands lead removal. These questions point up the apparent and growing conflict between the two policies of environmental protection and energy conservation.

The purpose of this discussion is to examine several aspects of the relationship between automobile emissions controls, lead antiknocks, and energy consumption. After presenting a brief review of the current status of EPA's regulations on the use of lead in gasoline, the following sections will examine (1) the impact of the regulatory process on the choice of a technical option which requires unleaded gasoline; (2) the effects of lead removal on the consumption of energy by automobiles; (3) the effects of lead removal on the economics of petroleum refining; and (4) the impact on consumer preferences for automobiles of an emissions control strategy which requires unleaded gasoline.

Finally, it should be noted that the following discussion outlines some of the cost implications of lead removal without presenting any evaluation of the benefits of a reduction in lead emissions. In a complete cost-benefit analysis estimates of both costs and benefits are compared to each other. For the purpose of definition, "costs" refer to the net increase in the expenditure of resources stemming from the implementation of lead additive controls. "Benefits"

refer to the reduction in the social costs or damages of lead pollution to public health, crops, animals, materials, and aesthetics. In this regard it is important to point out that the benefits--measured in terms of (1) a reduction in the number of lead poisonings; (2) a reduction in the number of individuals with elevated blood lead levels; or (3) a reduction in environmental effects--of lead removal have never been assessed.

#### 1.1 The Current Status of Regulations for Controlling the Use of Lead Additives in Gasoline

The 1970 Amendments to the Clean Air Act (Clean Air Amendments) provided the Environmental Protection Agency with the means to establish a stringent program for controlling automobile air pollution. This legislation ordered EPA to implement automotive emissions standards beginning with 1975 model cars that are 90 percent lower than federal standards for 1970 cars. To insure that these standards would be achieved, Congress added provisions authorizing federal regulation of fuels and fuel additives.

Under the law EPA may control or prohibit the manufacture and sale of any fuel or fuel additive for use in motor vehicles for two reasons: (1) if the emissions products of

the fuel or fuel additive endanger the public health; or (2) if the emissions products of the fuel or fuel additive significantly impair the performance of any emissions control device which is in general use, or which has been developed to the point where within a reasonable time it would be in general use (Clean Air Amendments, 42 U.S.C. at §1857f-6c(c) (1) (1970)). EPA used both of these criteria in implementing regulations on the use of lead additives.

In the initiation of regulatory action to require the general availability of unleaded gasoline, EPA first made a technical assessment of the emissions control devices under consideration by automobile manufacturers for meeting 1975-76 standards. EPA is required by the Clean Air Act to consider scientific data including a cost-benefit analysis comparing control devices which are likely to be in general use and which require control or prohibition of lead additives in gasoline. The major conclusions of the cost-benefit study (Aerospace Corporation, 1971) were:

- (1) All control systems that major automobile manufacturers were planning to use for meeting 1975-76 emissions standards incorporated catalytic converters.
- (2) The emissions products of lead additives (even in small amounts) in gasoline greatly reduced

the catalyst's ability to control emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxides.

- (3) Lead traps for removal of lead particulates from exhaust gases prior to passage through the catalyst were not effective in preventing damage to the catalyst.
- (4) Unleaded gasoline should, therefore, be made available in sufficient quantities to satisfy the demands of vehicles equipped with catalytic converters.

Accordingly, EPA concluded that without regulator action the supply of unleaded gasoline would be uncertain in all parts of the country and may be insufficient to assure protection of catalytic devices. The Agency has required that beginning July 1, 1974, all gasoline retailers who sell more than 200,000 gallons of gasoline annually must offer for sale one grade of unleaded gasoline (Federal Register, 1973b). This group includes about 160,000 service stations or approximately 45 percent of the branded retail outlets in the U.S.

Although the regulation does not authorize explicit penalties for retailers who fail to offer unleaded gasoline for

sale, it does specifically prohibit retailers from putting leaded gasoline into any motor vehicle which has been labeled "unleaded gasoline only". Labels of this kind will appear on automobiles that have been equipped with lead sensitive emissions control devices.

In contrast to the technical basis for ordering unleaded gasoline, EPA's phased reduction plan is based entirely on public health considerations. On the basis of an evaluation of scientific and medical information, the Agency has concluded that environmental lead exposure is a major public health problem (U.S. Environmental Protection Agency, 1972). Present levels of lead exposure constitute a sufficient risk of adverse physiological effects for a small but significant portion of the urban adult population and up to 25 percent of the children in urban areas (Federal Register, 1973c).

Lead exposure is caused by a combination of sources including lead in the air, food, water, leaded paint, and street dust. Although EPA has stated that it is difficult to determine which source(s) is (are) the most significant from a health standpoint, lead from the combustion of gasoline has accounted for over 90 percent of the tonnage of lead emitted into the air (R. E. Engel, et al., 1971). Lead from gasoline combines with lead from other sources to



create high lead levels in urban soils and dusts. But of all of the sources of lead, lead from gasoline is currently the largest and most ubiquitous source of lead in the air, dust, and dirt in urban areas.

The phased-reduction schedule will prohibit refiners from exceeding a specified average lead content per gallon. Each refinery will be permitted to average its lead usage over the quarterly production of all grades--regular, premium, and unleaded--of gasoline. The average lead content of the total pool must not exceed the total pool standard which will decline over a five-year period (Table 58).

The objective of the phased-reduction schedule is to reduce by 60-65 percent the 1971 level of lead utilization in gasoline.

Table 58 summarizes the proposed and revised regulations for lead additives. The 1974 data for introducing unleaded gasoline correspond to the beginning of the new model year for 1975 automobiles. The revised phased-reduction schedule which averages over all grades of gasoline has been moderated somewhat in the early years but extended for an additional year through 1979. (This will be discussed in greater detail in 1-4 ).

EPA has granted an automobile industry request for a one-year suspension of the 1975 emissions standards. In



Table 58

U.S. Environmental Protection Agency Restrictions on the Lead  
Content of Gasoline

(TEL contents in grams per gallon)

Research Octane Number	1974	1975	1976	1977	1978	1979	1980
Unleaded 91 <sup>a</sup>	0.05 <sup>b</sup>	0.05	0.05	0.05	0.05	0.05	0.05
Regular 94 <sup>c</sup>	-	2.00	1.70	1.50	1.25	1.25	1.25
Premium 100 <sup>c</sup>	-	2.00	1.70	1.50	1.25	1.25	1.25
Regular 94 <sup>d</sup>	-	1.70	1.40	1.00	0.80	0.50	0.50
Premium 100 <sup>d</sup>	-	1.70	1.40	1.00	0.80	0.50	0.50

<sup>a</sup> The octane requirement for unleaded gasoline is not less than 91 Research Octane Number

<sup>b</sup> The federal regulation defines "unleaded gasoline as gasoline containing not more than 0.05 grams of lead per gallon and not more than 0.005 grams of phosphorus per gallon. Phosphorus emissions products also cause deterioration of catalytic devices.

<sup>c</sup> Proposed on January 10, 1973 (National Refiners' Association, 1972)

<sup>d</sup> Finalized on December 6, 1973 (Federal Register, 1973c)

granting the suspension the Agency implemented two sets of interim standards, one for California and one for the rest of the U.S. (see Appendix A )(William Ruckelshaus, 1973). The emissions levels in the California interim standards will necessitate the installation of catalytic converters in 1975 model cars sold in that state, or about 10 percent of all cars sold in the U.S. As a result of EPA's decision on interim standards, General Motors, whose share of the new car market exceeds 50 percent, plans to install catalytic devices on most of its 1975 models. Consequently, about 60 percent of the 1975 model cars will be equipped with catalysts, which, for proper operation, will require unleaded gasoline.

The widespread installation of catalytic converters and, hence, the national need for unleaded gasoline may be a short-run phenomenon. The installation of catalysts and exclusive use of unleaded gasoline in all post-1974 cars would have meant a complete phase-out in the demand for leaded gasoline in about 10 years. However, the recent demonstration of lead tolerant control systems that can meet federal emissions standards, for example, the Wankel and stratified-charge engines, may ultimately eliminate the need for unleaded fuel.

In anticipation of the mass production of lead tolerant systems beginning in the late 1970's, EPA has now made the phased-reduction schedule its long-term weapon for controlling automotive lead pollution. In order to insure that lead emissions from these new technology cars will not endanger public health, the Agency lowered by 60 percent (from 1.25 to 0.50 grams per gallon) its 1979 standards for maximum allowable lead content of gasoline.

The recent problem of shortages in energy supplies has brought about a reconsideration of several environmental protection measures including the automobile emissions standards. The engine adjustments and add-on devices that auto makers have installed since 1970 have already reduced vehicle fuel economy substantially. Although Detroit has said otherwise, the installation of catalytic converters may bring additional losses in fuel economy. Because the shortages in the supplies of gasoline and fuel oil are especially acute, EPA may be forced to delay the implementation of any automobile emissions control that decreases fuel economy.

As an energy conserving measure, Congress is considering at this time giving the automobile manufacturers another postponement in EPA's current timetable for eliminating automobile pollution. The Senate already has voted to give

the auto industry a one-year extension in the 1975 standards. If this extension is authorized, fewer 1976 model cars would require catalytic converters, and hence, the necessity for unleaded gas would be diminished even further. This delay would also give the auto industry additional time to introduce into mass production new engine lines, for example, the Wankel and stratified-charge engines, that can meet emissions standards and burn leaded gasolines. The long-term effect of a Congressional postponement in EPA's timetable may lessen the importance of unleaded gasoline in controlling automobile air pollution.

The future status of the phased-reduction schedule is also uncertain. Industry has challenged EPA's claim that lead in gasoline is a health hazard. During public hearings on the phased-reduction proposal, the National Petroleum Refiner's Association (1972), the International Lead Zinc Research Organization (1973), and the major producers of lead antiknocks, Ethyl Corporation (1972), and duPont (1973), all testified that available medical and scientific evidence did not support the view that emissions products from the combustion of lead antiknocks are hazardous to human health. Ethyl, duPont, PPG, and Nalco Chemical have filed separate petitions in U.S. Court of Appeals requesting that the court review and ultimately set aside EPA's basis for removing lead

in gasoline.

The National Resources Defense Council has also challenged the EPA phased-reduction schedule. NRDC has filed a petition in the U.S. Court of Appeals which requests that the court order EPA to implement a more restrictive phased-reduction schedule.

The phased-reduction issue is further complicated by the energy implications of lead removal. The current shortages in the demand for gasoline are due to a nationwide shortage of refining capacity. Lead removal will add to this dilemma by requiring the construction of an even larger increment of refining capacity to produce the same volume of gasoline but with less lead.

## 1.2 The Regulatory Perspective and the Technical Basis for Unleaded Gasoline

The automobile manufacturers' commitment to use catalytic converters on 1975 cars has provided the Environmental Protection Agency with the technical basis for ordering the general availability of unleaded gasoline. The manufacturers' decision to use catalysts reflects the technical and economic constraints which face the industry as well as the legislative and regulatory constraints which have been imposed by Congress and EPA.



From the purely technical standpoint the complex and interdependent relationships between automotive engine design, fuel composition, and exhaust characteristics offer the manufacturers several options for controlling emissions. Some of the possibilities include: (1) modifications in the internal combustion engine plus after-treatment devices for the exhaust system; (2) major engineering changes in the internal combustion engine and carburetion system; and (3) the development of entirely new low emissions power systems to replace the internal combustion engine.

In its response to pre 1975-76 California and federal emissions standards, the automobile industry has adopted a strategy of adding on emissions control devices and making minor engine adjustments. This kind of strategy is due in part to the industry's determination to preserve as much of the technology of the internal combustion engine as possible, and it is due in part to the industry's desire to protect its investment in plant and capital for producing internal combustion engines.

Since 1970 domestic automobile manufacturers have maintained that slight adjustments in the internal combustion engine plus the installation of after-treatment devices would be the only feasible technical option for meeting the 1975-76 emissions standards. Although Detroit has never ruled



out the possibility of developing a practical, low emissions alternative to replace the internal combustion engine, the manufacturers have testified that the short timetable for compliance which is specified in the Clean Air Amendments did not permit sufficient lead-time to mass produce an entirely new engine (U.S. Congress, 1970).

In 1970 before passage of the Clean Air Amendments, the automobile manufacturers were considering two basic types of exhaust reactors for installation on 1975-76 production models. These were: (1) the thermal reactor, a high temperature chamber which is attached to the engine and completes the oxidation of hydrocarbons and carbon monoxide; and (2) the catalytic converter, a muffler-like device which is attached to the tailpipe and, depending on the type, either oxidizes hydrocarbons and carbon monoxide or reduces nitrogen oxides. A third kind of device, the exhaust gas recirculation system, has already been installed on 1973 model cars to meet 1973 nitrogen oxide standards. This device is a special tailpipe for cooling and recirculating part of the exhaust gases back through the intake manifold.

Because the effectiveness of all of these add-on systems is reduced by the presence of lead in the exhaust, the auto makers asked Congress to provide for the production

and distribution of unleaded gasoline. During 1970 hearings before the California Air Resources Board (1970) and before the Senate Subcommittee on Air and Water Pollution (1970), General Motors and Ford presented evidence describing the deleterious effects of the emissions products of lead additives on emissions control devices. For example, the high alloy metal and ceramic materials in the thermal reactor corrode more rapidly when the emissions products of lead additives and phosphorus are present in the exhaust.\*

The effectiveness of the catalytic system deteriorates very quickly because lead particles and compounds adhere to the surfaces of the active catalytic ingredients. The effectiveness of the exhaust gas recirculation system is also reduced because lead deposits form at temperatures above those desired for nitrogen oxide prevention and affect the air-flow characteristics of the system. In the auto industry's opinion, unleaded gasoline was an essential requisite if the potential of these control devices were to be fully developed.

Earlier in 1970 the industry had strengthened its position with respect to its demands for unleaded gasoline. In February General Motors announced that it would lower the

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\*Lead levels apparently do not affect reactor durability as long as the levels of phosphorus in fuel are low (The Oil and Gas Journal, 1972).

compression ratios in its 1971 and later model cars in preparation for the 1975-76 emissions standards; engines with lower compression ratios would be able to run on lower octane unleaded fuels (The New York Times, 1970). Within a month Ford and Chrysler followed with similar announcements. These announcements essentially placed the burden on the petroleum companies and on the government to provide a fuel that would be compatible with the kind of emissions control system Detroit had in mind for 1975-76.

During 1970 the automobile industry's relatively active approach to the legislative and regulatory process represented a significant departure from its previous behavior toward government regulation of its products. According to White (Lawrence J. White, 1971), before 1970 the industry generally had resisted any regulatory attempts either to curb automobile air pollution or to increase passenger safety. In the face of regulatory constraint the auto companies had often dragged their feet and had resisted the imposition of government restrictions altogether.

Then on the eve of the introduction of stringent and comprehensive anti-pollution legislation in California and in the U. S. Congress, the industry began a concerted and coordinated effort to shape the regulatory decision-making process to fit its assessment of the market for American cars.

Bain (1970), who has analyzed the behavior of the auto industry in the face of regulatory constraints, offers the following explanation for this change:

By 1968 or 1969, with rapidly developing California and federal legislative action to regulate automotive air pollution, American automakers were in a position that favored their developing a concerted general strategy for coping positively with regulatory constraints it faced or was about to face--a strategy that would put them in the driver's seat in selecting specific reactions to regulatory pressures, while still leaving room for about as much nonprice rivalry as they desired. The high concentration of the industry together with the existence of a common "opponent" made the adoption of such a positive strategy feasible.

The Amendments to the Clean Air Act which finally passed Congress in late 1970 were much more stringent than the automobile manufacturers had anticipated. At the last minute Senator Muskie added the now famous mandate to the law requiring 1975 model cars to reduce emissions of hydrocarbons and carbon monoxide by 90 percent of the emissions allowable from 1970 cars and 1976 model cars to reduce emissions of nitrogen oxides by 90 percent of the emissions allowable from 1971 cars.

The requirement that 1970 emissions standards be reduced by 90 percent was derived from a short paper published in mid 1970 by Barth, et al., of the National Air Pollution Control

Administration. The automobile industry had assumed that the standards developed in the NAPCA paper (see Table 59) would become goals for 1980 (Jude Wanniski, 1973).

The automobile manufacturers strenuously objected to the 90 percent reductions on the grounds that they knew of no technical means for achieving them. Since then the automakers have put massive resources into a crash program to develop systems that can meet the 1975 and 1976 standards. In 1972 General Motors alone spent \$248 million and employed 4,000 people in developing emissions controls (Business Week, 1973).

In this race catalytic systems appear to have had some technical advantages over the thermal reactor. One difficulty in the thermal reactor has been achieving a high enough temperature to burn up engine hydrocarbon and carbon monoxide emissions. This problem may be remedied by increasing the richness of the air-fuel mixture, but rich reactor systems have a much higher fuel penalty and more severe durability problems. Another difficulty arises from the fact that the thermal reactor alone cannot achieve both the 1975 and 1976 standards. For 1976 the reactor must be coupled with a catalytic converter in order to achieve the required nitrogen oxide levels.



Table 59

## Automobile Emissions Standards

Requirements <sup>a</sup>	HC	CO	NO <sub>x</sub>
1. California (1974)	1.5	23.0	1.3
2. California (Proposed 1975 Standards) <sup>b</sup>	0.5	12.0	1.0
3. HEW (Proposed 1975 Standards) <sup>b</sup>	0.5	11.0	0.9
4. HEW (Proposed 1980 Goals) <sup>c</sup>	0.41	6.16	0.40
5. EPA (1975-76) <sup>d</sup>	0.41	3.40	0.40

<sup>a</sup> Emissions Requirements in grams per mile

<sup>b</sup> U. S. Senate, Committee on Public Works, Subcommittee on Air and Water Pollution (U.S. Congress, Senate, 1970)

<sup>c</sup> Barth et al. (1970)

<sup>d</sup> Adopted (Federal Register, 1972)



Rather than attempt to develop two systems for 1975 and 1976, the manufacturers have preferred to concentrate on those 1975 control systems that can be modified to achieve greater nitrogen oxide control needed in 1976. In this regard the catalytic converter has an advantage because it can be used as an oxidizing agent for hydrocarbons and carbon monoxide or as a reducing agent for nitrogen oxides. The control system for 1976 on which most development effort has been concentrated is the dual catalytic system.

The National Academy of Sciences Committee on Motor Vehicle Emissions (CMVE) (1973) recently reviewed the state-of-the-art progress toward meeting the 1975-76 standards. The committee reported that four types of systems will meet the 1975 model year light-duty motor vehicle emissions standards during certification testing. These are: (1) the modified conventional engine equipped with an oxidation catalyst; (2) the carbureted stratified-charge engine; (3) the Wankel engine equipped with a thermal reactor; and (4) the diesel engine. Only the catalytic system requires unleaded gasoline for effective operation; the other three systems do not.

The Committee also determined that five systems, which are in the early stages of development, have met the 1976

standards at low mileage levels; all five of these incorporate catalytic devices. They are: (1) the modified conventional engine equipped with dual catalysts; (2) the modified conventional engine equipped with dual catalysts and a thermal reactor; (3) the modified conventional engine equipped with a reduction catalyst and two thermal reactors; (4) the modified conventional engine equipped with a three-way catalyst and electronic fuel injection; and (5) the stratified-charge engine equipped with an oxidation catalyst. All five of these systems would require unleaded gasoline for effective performance.

Of the four systems that meet the 1975 standards, Detroit is responsible for the catalytic system. A sufficient number of cars equipped with catalytic converters could be produced to meet the 1975 new car demand. The other three systems, Wankel, stratified-charge and diesel engines, have been developed outside the U.S. In 1975 the combined production of automobiles with these systems will probably only account for about 5 percent of new car sales in the U.S.

The Wankel engine which currently is being mass-produced in Japan and sold in the U.S. has a sales projection of 350,000 cars for 1975. General Motors has begun ordering parts and machine tools to produce about 100,000 Wankel

engine powered cars in 1975 (Wall Street Journal, 1973a).

Honda Motor Company also of Japan plans to introduce the stratified-charge engine in the U.S. in 1975. Both Ford (Wall Street Journal, 1973b) and Chrysler (Wall Street Journal, 1973c) have purchased the rights to the Honda technology. In Senate hearings Ford also offered to produce 500,000 stratified-engine powered cars in 1977, if Congress would ease the nitrogen oxide emissions requirement in the Clean Air Amendments (U.S. Congress, 1973).

The CMVE report contained reservations about the use of catalytic systems particularly in meeting the 1976 standards. The dual catalyst, a system which will most likely be mass produced by domestic manufacturers, is the most disadvantageous system in terms of cost, fuel economy, durability and maintenance. The stratified-charge engine which will not be available in large numbers until late in the 1970's is superior to the catalyst in all categories.

With respect to the use of catalysts CMVE expressed concern that strict enforcement of the provisions of the Clean Air Act might force the adoption of the control system first to be developed and certified and thereby defeat a goal of the earliest possible attainment of compliance by a means of control that costs less, has greater durability,

and achieves better fuel economy. This point is especially important because once the automobile industry has committed itself to the production of a catalyst-dependent control system, the industry will continue to produce them for a number of years instead of switching to a more economical system.

The same kind of concern must also be expressed for the adoption of a system that requires unleaded gasoline. If strict enforcement of the Clean Air Act forces the adoption of a system that cannot tolerate the emissions products of lead additives, then it might defeat the goal of developing a means of control that will tolerate less expensive fuels. In this case the commitment to a lead sensitive system will require the petroleum industry to commit large investment expenditures for the capacity to produce unleaded gasoline.

### 1.3 The Energy Effects of Lead Removal

The energy requirements for automotive transportation have grown tremendously since 1950, with the result that the family car now consumes more energy than all other modes--passenger and freight--of transportation combined. In 1971 the use of the automobile for passenger transportation alone absorbed over 69 billion gallons of motor fuel. This repre-

sents slightly more than 50 percent of energy consumed by transportation activities (Table 60). The 1971 percentage represents an accumulated increase from 1950 of nearly 15 percent in the size of the relative share of transportation energy devoted to the automobile.

Transportation as a whole is heavily dependent on petroleum energy; petroleum supplies well over 90 percent of all energy consumed by transportation. As the data in Table 61 indicate, the automobile uses about 53 percent of petroleum energy devoted to transportation, or about 28 percent of all petroleum consumed in the U.S.

Because of the enormous energy demands of the automobile, any reductions in vehicle fuel economy, either from emissions controls or from restrictions on the use of lead, will have an adverse impact on total energy consumption.

Many factors including vehicle characteristics, engine specifications, emissions control systems, and driving habits affect automotive fuel economy. The primary vehicle characteristics which contribute to fuel economy differences between cars include vehicle size and weight, type of transmission, and number of additional power accessories. Of these vehicle size and weight are the most significant; the larger, heavier vehicles have greater frontal areas and require larger engines to equal the acceleration levels of



Table 60  
Energy Consumption by Personal Passenger Cars in the U.S.

Year	Personal Passenger Cars <sup>a</sup> (10 <sup>3</sup> )	Fuel Consumption by Passenger Cars <sup>a</sup> (10 <sup>6</sup> gallons)		Fuel Consumption for All Motor Vehicle Transportation <sup>a</sup> (10 <sup>6</sup> gallons)		Energy Consumption for All Transportation <sup>b</sup> (10 <sup>12</sup> Btu)	
		Personal Passenger Cars	All Passenger Vehicles	Percent to Passenger Cars	All Motor Vehicles	Percent to Passenger Cars	Total
1950	40,311	24,305	25,037	97.1	37,603	66.3	8,616
1955	52,092	33,548	34,319	97.8	51,865	64.7	9,837
1960	62,258	41,169	41,996	98.0	57,878	71.1	10,988 <sup>c</sup>
1965	76,643	49,723	50,598	98.3	71,104	69.9	12,733
1970	89,280	65,649	66,728	98.4	92,238	71.1	16,469
1971	92,799	69,213	70,461	98.3	97,547	71.0	17,119

<sup>a</sup> Federal Highway Administration (U.S. Department of Transportation)

<sup>b</sup> U.S. Bureau of Mines (U.S. Department of the Interior)

<sup>c</sup> Assuming 125,000 Btu/gallon of gasoline

<sup>d</sup> For 1961



Table 61

## Petroleum and Passenger Car Energy Consumption in the U.S.

Year	Petroleum Consumption for All Transportation (10 <sup>12</sup> Btu)		Petroleum Energy Consumption (10 <sup>12</sup> Btu)		
	Total <sup>a</sup>	Percent to Passenger Cars <sup>b</sup> , <sup>c</sup>	Total <sup>a</sup>	Percent to Transportation	Percent to Passenger Cars <sup>b</sup> , <sup>c</sup>
1963	11,506	49.2	21,950	52.4	25.8
1965	12,179	50.7	23,241	52.4	26.6
1967	13,542	51.0	25,335	53.4	27.2
1969	15,290	51.0	28,419	53.8	27.4
1970	15,720	52.2	29,614	53.1	27.8
1971	16,330	53.0	30,649	53.3	28.4

<sup>a</sup> U. S. Bureau of Mines (U.S. Department of the Interior b)<sup>b</sup> Federal Highway Administration (U.S. Department of Transportation)<sup>c</sup> Assuming 125,000 Btu/gallon of gasoline

smaller cars.

Of the different engine specifications, for example, compression ratio, displacement, and air-fuel ratio, that influence fuel economy, it is well established that an increase in compression ratio--holding all other specifications constant--will produce better gasoline mileage. Increases in compression ratio up to 14:1 will produce increases in an engine's ability to do work with greater efficiency or with greater power per gallon of gasoline consumed.

As compression ratio increases, the corresponding motor fuel octane number must also increase. Octane number is a measure of the ability of a fuel to resist engine knock. Knocking occurs when engine temperatures cause the air-fuel mixture to ignite prematurely, and the presence of knocking indicates inefficient engine operation in terms of fuel consumption. Because engine temperature and engine efficiency both increase with increases in compression ratio, engine knock also places an upper limit on efficient engine design. Figure 108 illustrates a relationship between octane number and the amount of work an engine can do.

In the 15 years preceding 1971, increases in compression ratio have probably offset losses in fuel economy due to increases in vehicle weight and to the number of installed

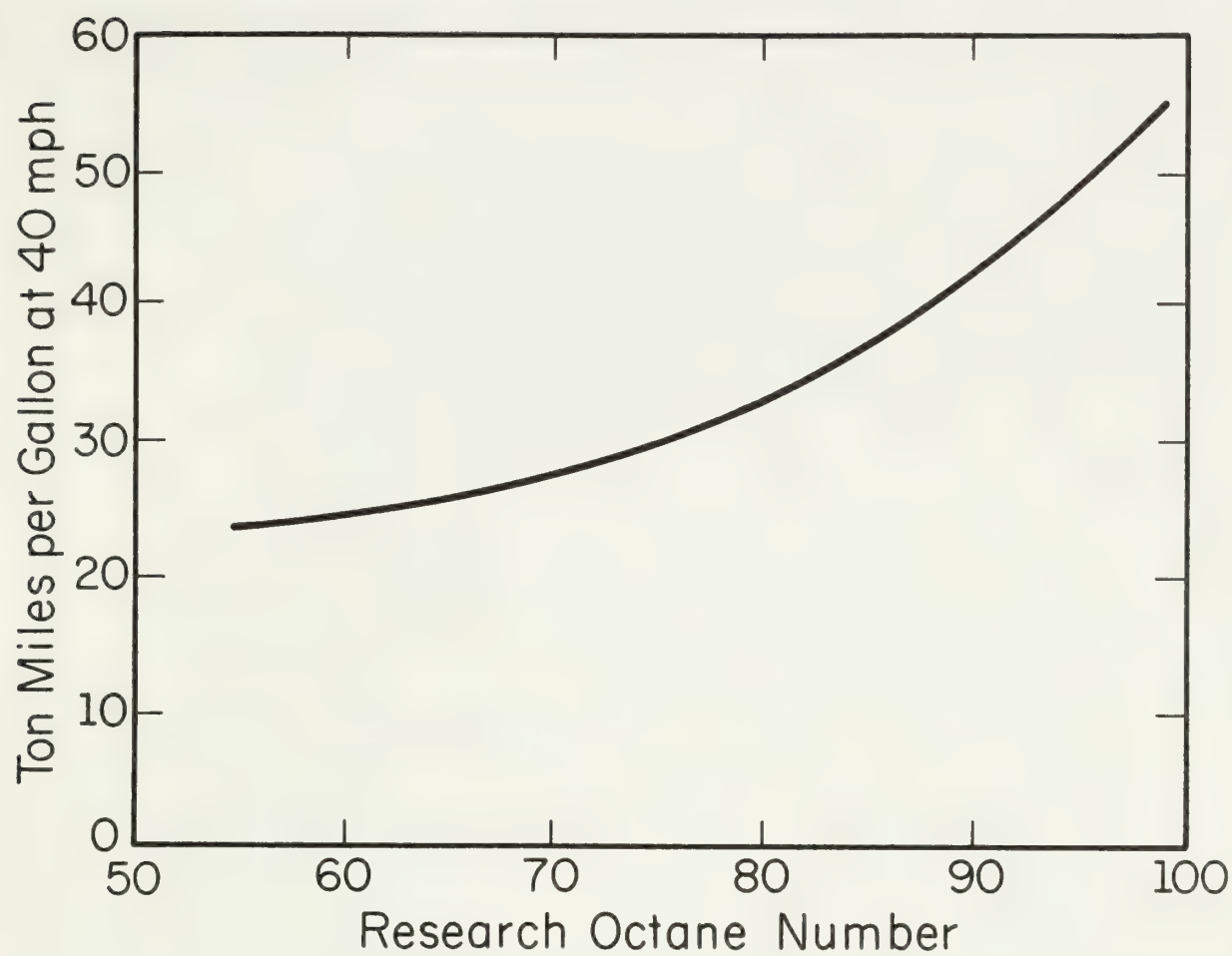


Figure 108

Engine Performance Per Gallon of Fuel at Specific Octane Levels<sup>a</sup>

<sup>a</sup>Enos, 1962.

power accessories. During this period compression ratios steadily increased on all production model cars from a sales-weighted average of 9.13:1 in 1956 to 9.27:1 in 1970 ( Ward's \_\_\_\_\_ Automotive Yearbook). Although national average fuel economy did not increase during this period, it declined only slightly from 14.16 to 13.57 miles per gallon, about 4 percent (U.S. Department of Transportation). This decline is very small in view of the fact that manufacturers were building heavier cars and equipping more of them with air conditioners, automatic transmissions, power brakes, and power steering.\*

In 1971 Detroit began to reduce compression ratios to accommodate low octane unleaded gasoline in preparation for the introduction of lead sensitive catalytic converters in 1975 and 1976. On a sales-weighted basis, the average compression ratio of all cars dropped from 9.27:1 to 8.65:1 in \_\_\_\_\_

\*Between 1956 and 1970 the sales-weighted average curb weight for domestic automobiles increased 7 percent (from 3,280 to 3,520 pounds). In 1956 only 2.8 percent of new car production had factory installed air conditioning; 27.7 percent had power steering; and 74.8 percent had automatic transmissions. By 1970 these figures had increased to 63.4 percent, 82.5 percent and 91.1 percent respectively (Ward's \_\_\_\_\_ Automotive Yearbook).

in 1971. Compression ratios were reduced again in 1972 to 8.45:1 and in 1973 to 8.3:1 on a sales-weighted average.

Based on measurements of the fuel economy of new cars, La Pointe (1973) has reported that the 1971 drop in compression ratios has resulted in an accumulated loss in fuel economy of 4.5-4.9 percent over uncontrolled cars, or a 3 percent loss compared to 1970 production models. The overall drop in compression ratios from 9.27:1 to 8.3:1 should increase gasoline consumption by 6-8 percent.

Finally, the future development of a lead tolerant emissions control system that is able to meet federal standards might provide some improvement in vehicle fuel economy. Although a lead tolerant system would allow the automobile manufacturers to increase compression ratios, EPA's phased-reduction schedule may prevent a complete restoration of compression ratios to pre-1971 levels. In other words, the severity of the phased-reduction schedule may impede the future development of an economic and energy conserving lead tolerant emissions control system.

Losses in fuel economy from increased vehicle weight and emissions controls plus a larger number of vehicles on the highway have caused the national demand for gasoline to increase very rapidly in the last few years. The demand for



gasoline has grown much faster than the petroleum industry's capacity to refine the necessary supply. At the present time a deficiency in domestic refining capacity is the main reason for persistent shortages in gasoline and fuel oil.

Unless vehicle fuel economy improves significantly in the next few years, the consumption of gasoline will continue to grow at a rapid rate through the 1970's. Several projected rates of growth in gasoline consumption are listed in Table .

The USEPA projections in Table 62 served as the basis for the Bonner and Moore (1971a) analysis of the economic effects of removing lead from gasoline. These projections which were obtained from equations supplied by EPA indicate that without emissions controls, the demand for gasoline would grow at an annual rate of 2.8 percent during the period 1971-80. With emissions controls national demand would grow at an average annual rate of 3.4 percent over the same period. The difference in the two projections, 0.6 percent, will amount to over 29 million gallons of gasoline more per day in 1980.

EPA's projections of the gasoline demand are extremely conservative. In actuality domestic consumption of gasoline has been increasing at an average annual rate of about 5 percent. If this trend continues, the increase in daily consumption in 1980 will be over 74 million gallons. Assum-



Table 62

Projections of Annual Rates of Growth in the Demand for Motor  
Fuel in the U.S.

Year	USBM <sup>a</sup> (actual)	USEPA <sup>b</sup>	TMS <sup>c</sup>		NPC <sup>d</sup>
			Cal.	Fed.	
1965-70 (average)	4.8	-	-	-	-
1971	4.0	-	4.6	4.6	-
1972	6.3	3.9	4.2	4.2	-
1973	5.0 <sup>e</sup>	3.8	3.9	3.9	-
1971-80 (average)	-	3.4	3.1	3.7	3.4

<sup>a</sup> U. S. Bureau of Mines (U.S. Department of the Interior b)

<sup>b</sup> Bonner and Moore Associates (1971a)

<sup>c</sup> Turner, Mason, and Solomon (1972)

<sup>d</sup> National Petroleum Council (1972)

<sup>e</sup> January through October 1973

ing that emissions controls are responsible for 60 percent\* of the increase in demand, this will amount to a daily increase of about 45 million gallons or one and one-half times the increase predicted by EPA (see Table 63).

To summarize, in preparation for the use of lead sensitive catalytic converters, automobile manufacturers have reduced engine compression ratios to accommodate lower octane unleaded gasolines. The net result of all of the changes required for vehicle emissions control has been a reduction in vehicle fuel economy. In view of the enormous amounts of petroleum energy consumed by automobiles, automotive emissions controls plus restrictions on the use of lead in gasoline are having an adverse impact on total energy consumption in the U.S.

#### 1.4 The Economic Effects of Lead Removal on the Domestic Petroleum Industry

If fully implemented, EPA's regulations for reducing the use of lead in gasoline will have a significant economic impact on a number of sectors in the petroleum industry. The most important economic effect of lead removal will be the

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\*This estimate comes from La Pointe's (1973) analysis.

Table 63

Estimates of Increased Consumption of Energy Resources  
(10<sup>3</sup> Barrels/day)

<u>Consumption of Gasoline</u>	<u>1972</u>	<u>1980</u>
(1) USEPA Reference Schedule <u>a</u>	6,145	7,671
(2) USEPA Forecast <u>a</u> Increase for Emission Control	6,223	8,376 705 9.2
(3) Forecast based on Present Growth Rate <u>b</u> Increase for Emission Control <u>c</u> Percent	6,394 <sup>d</sup>	9,447 1,067 13.9
 <u>Consumption of Crude Oil</u>		
(1) USEPA Reference Schedule <u>a</u>	12,476	17,964
(2) USEPA Forecast <u>a</u> Increase for Emission Control Percent	12,509	18,507 543 3.0
(3) Forecast based on Present Growth Rate <u>e</u>	16,602	25,652

a Bonner and Moore (1971a)

b Data on gasoline consumption from the U.S. Bureau of Mines (U.S. Department of the Interior b) indicate an annual growth rate of 4.8 percent. Federal Highway Administration (U.S. Department of Transportation) data for highway motor fuel consumption indicate a 5.3 percent annual growth rate. A 5.0 percent rate was used in making these estimates.

c 60 percent of the increased consumption

d 1972 average daily consumption of gasoline (U.S. Department of the Interior b)

e U.S. Bureau of Mines (U.S. Department of the Interior b) data on the total disposition of crude oil indicates a 5.4 percent annual growth rate

necessity to increase the level of capital expenditures for new refining capacity. This requirement will eventually lead to increases in the unit costs of producing both unleaded and conventional grades of gasoline, and it will affect the economics of refining other products such as fuel oil and petrochemical feedstocks. In addition to the refining sector, lead removal will require the procurement of larger supplies of crude oil and the investment of additional capital in distribution and marketing facilities.

Gasoline is potentially by far the most valuable product obtained from crude oil, and U. S. refiners have for decades developed processes which have increased the octane rating and output of gasoline per barrel of crude oil. Cracking processes such as hydro, catalytic, and thermal, for example, break heavier petroleum molecules into smaller more volatile components in the gasoline range, and synthesizing processes such as catalytic reforming\* and alkylation\*\* produce higher octane hydrocarbons for blending.

Under the present state of technology in petroleum

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\*Reforming is a process that converts low octane, straight-run naphtha distillates into aromatics by molecular rearrangement and cracking.

\*\*Alkylation is a process that adds alkyl radicals to olefins to produce saturated branched parafins.

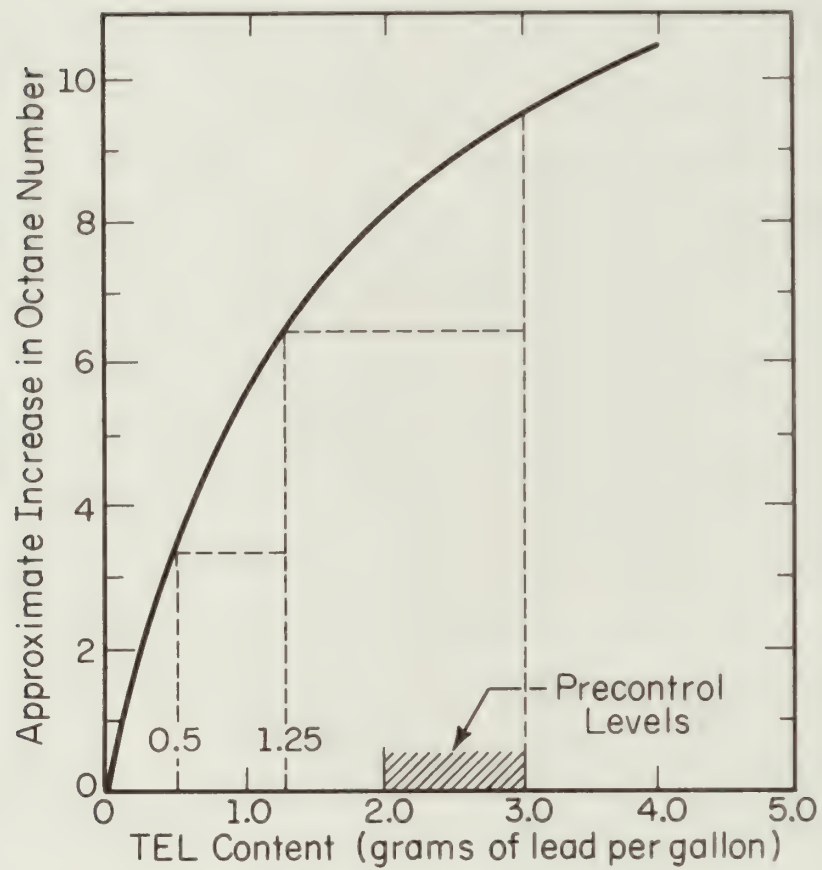
processing, adding tetraethyl lead (TEL) provides refiners with the most economic means of producing high octane gasolines in the 94-100 RON range. Regular and premium grades of gasoline typically have clear octane ratings of 86-88 and 92-94 RON respectively. Octane ratings can be increased by 6-8 octane numbers by adding 2.1-2.4 grams of lead per gallon to regular and 2.6-2.8 grams per gallon to premium. These figures represent a range of average annual concentrations of lead added to gasoline since 1965. The actual amount of lead that is in gasoline at any one time varies considerably depending on the season of the year and on the region of the country (U. S. Department of the Interior a).

Figure 109 illustrates the technical relationship between the concentration of TEL and the octane number in a typical gasoline. As the graph indicates, successive increments of TEL added to gasoline produce smaller increases in octane rating.

The production of higher octane unleaded gasolines is more expensive in terms of crude oil and refinery energy requirements. Without lead refiners must increase clear octane ratings by blending in larger quantities of the higher octane hydrocarbons such as branched-chain paraffins and aromatics. In very general terms this means that the amount



FIGURE 109. Approximate Relationship between  
Tel Content and Increase in Octane Number.





of alkylation and reforming processing must be increased for a given crude oil throughput. More extensive operation of these processes also requires additional process heat, steam, and electricity.

Bonner and Moore (1971a) have estimated that the production of unleaded gasoline of 91 RON or greater coupled with EPA' phased-reduction schedule will necessitate increasing the national clear pool octane rating from 88.4 in 1971 to 91.5 RON in 1980. To achieve this increase the petroleum industry must expand its present refining capacity for synthesizing high octane hydrocarbons.

The Bonner and Moore (1971a) study also estimated that automobile emissions controls coupled with EPA's lead removal strategy would require the petroleum industry to make a net cumulative increase in investment expenditures of \$2.5 billion by 1980. This figure represents a total increase of \$5.7 billion for investments in new plants (\$2.7 billion) and marketing facilities (\$3.0 billion) minus a reduction of \$3.2 billion in reduced costs of refining due to smaller purchases of tetraethyl lead. On a cost per gallon basis this will mean an increase in cost of about .25 cents per

gallon to produce and distribute unleaded gasoline.\*

These estimates probably understate the costs of lead removal for the following reasons. The Bonner and Moore (1971a) study technique employed linear programming models to determine the optimum response pattern of the refining industry to varying profiles of gasoline demand. As indi-

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\*In addition to the studies that have been prepared for USEPA there are several other published estimates of the cost of producing unleaded gasoline. A 1967 American Petroleum Institute study which was prepared by Bonner and Moore Associates (1967) estimated that unleaded gasoline would cost 1.8-4.7 cents per gallon more if all of the lead were removed immediately and the same octane requirements were maintained. A 1970 U.S. Department of Commerce Technical Advisory Committee report which was prepared by the Pace Company (1970) estimated the increase in production costs for seven different variations of pump strategy, TEL level, octane level, and gasoline purchasing patterns. The increases were between 0.17 and 4.22 cents per gallon. Finally in a later study Bonner and Moore (1971b) has estimated that the increase in the pump price for gasoline will be 1.5-2.0 cents per gallon, 0.2-0.9 cents per gallon in manufacturing and distribution costs plus the lost revenues from declining premium gasoline sales.

cated in the previous section, the demand projections for gasoline used in the Bonner and Moore study are very conservative. Consequently the estimates of additional investment expenditures and of the increase in the cost of refining gasoline are also conservative.

In addition all cost data incorporated in the Bonner and Moore study are based on 1970 prices. Although this is a sound basis for insuring consistency, domestic and world market prices of crude oil have increased dramatically due to factors which were not foreseeable in 1970. In order to obtain a more accurate estimate of the costs of lead removal, a new study should be made using current price data.

To determine whether the additional capital requirements will put an excessive strain on the petroleum industry, it is necessary to assess the industry's ability to finance new investment for all its needs. The petroleum industry is very capital intensive; capital expenditures for thirty leading American oil companies have been running at about \$10 billion annually for the last ten years (Richard C. Sparling and Norma J. Anderson, 1971). Table 64 provides data on the trends in investment expenditures by selected categories within the U.S. from 1961 to 1971.

Table 64  
Petroleum Industry Capital and Exploration Expenditures  
in the U.S.<sup>a</sup>  
(Billions of dollars)

	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971
Total Capital Expenditures	5.100	5.275	5.475	6.100	6.375	7.125	7.658	8.350	8.175	8.225	7.250
Crude Oil and Natural Gas Production	3.400	3.850	3.525	3.800	3.600	3.600	3.758	4.675	4.525	4.110	3.185
Percent of Total	66.7	67.2	64.4	62.3	56.2	51.0	49.0	56.0	55.3	50.0	44.0
Refineries	.360	.350	.325	.350	.600	.775	.775	.800	.950	1.075	1.050
Percent of Total	7.1	6.1	5.9	5.73	9.4	10.9	10.1	9.7	11.6	13.15	14.5
Marketing	.525	.600	.650	.850	1.000	1.100	1.250	1.150	1.250	1.450	1.350
Percent of Total	10.3	10.5	11.8	14.0	13.3	15.4	16.3	13.8	15.3	17.6	18.6

<sup>a</sup> Sparling (1971)

The industry clearly must increase its rate of investment in domestic refining capacity. For the past few years oil companies investments in new capacity have not kept pace with the growing demand for gasoline, and the current shortages in gasoline are due primarily to a shortage of refining capacity. At this time there is not a single new refinery under construction in the U.S. Although the petroleum industry spent over \$1.0 billion in 1971 on refineries that money was used to modernize and replace existing facilities.

The rate of additional investment in refining needed for the elimination of lead is dependent on how rapidly the phased-reduction schedule removes lead from conventional grades of gasoline. The Bonner and Moore study estimates that the total added costs for additional refining and marketing required by EPA's proposed reduction plan will run between \$250-300 million annually. The additional demands of the proposed plan are relatively mild compared to some of the other schedules that EPA has examined; milder impact on investment requirements clearly has been an important criterion for the selection of a phased reduction schedule.

In recent years domestic firms have spent only about 60 percent of their investment budgets in the U.S.; the balance is spent on exploration and development in Canada and overseas. Since 1968 capital expenditures made in this



country by the world's leading oil companies have declined. Investment in the U.S. is currently relatively less attractive than investment in foreign countries because the rate of return on average invested capital in the U.S. has declined since 1967 while it has increased for foreign countries. The current rate of return in the U.S. is significantly less than it is in the rest of the world (Richard C. Sparling, et al.). All of this indicates that because of the incentives, the petroleum industry may not be inclined to make extensive investments, particularly in refining, in the U.S. at this time.

In conclusion, petroleum refining is highly dependent on the economic and energy-saving benefits of utilizing TEL. EPA's regulations for lead removal will substantially reduce these benefits and will require new investment in refining capacity. Because these investments must be made at a time when there is a domestic deficiency in capacity to produce gasoline and fuel oil, lead removal will place an additional investment strain on the petroleum industry.

#### 1.5 The Cost Implications of Automobile Emissions Control for the Individual Customer

Automobile emissions control will mean higher costs to the consumer of automobile services for several reasons.



The initial cost of purchasing a new car will increase because of the installation of emissions control devices. Maintenance-related costs attributable to the maintenance of the emissions control system will increase. Finally operating costs will increase because of losses in fuel economy associated with emissions control and because of increases in the service station price of unleaded or low lead gasoline.

An assessment of the impact of the costs of emissions control on the consumer is important for two reasons. First the measurement of total costs that the consumer will pay for emissions control is one side of a cost-benefit analysis. Second, and more important for our purposes, these costs provide an indication of how consumers will react in terms of making new car purchases.

Studies by Aerospace (Aerospace Corporation, 1971), EPA (USEPA, 1970), and CMVE (National Academy of Sciences, 1973) have generated estimates of the costs of emissions control for a baseline vehicle with performance and fuel economy characteristics of a pre-control car, i.e., a car designed to operate on leaded gasoline. These studies estimated the initial costs of emissions control systems from manufacturing cost data for control system components. Equipment cost estimates were then added to increased operating costs to

determine the total costs of emissions control for an average vehicle lifetime.

The cost figures presented in these studies were stated in absolute terms, and they do not provide any information about the relative importance of the costs of emissions control to total expenditures for automobile transportation. Consequently, it is not possible to determine what implications these figures may have for the consumers' willingness to purchase new cars, or of greater importance, what implications they may have for the consumer's willingness to purchase smaller cars with greater fuel economy.

The above costs also have not accounted for the impact of increasing gasoline prices on total operating costs. An increase in the price of gasoline coupled with a decrease in fuel economy will have a multiplicative effect on increasing the costs of operating an automobile. For example, an increase of 10 percent in the pump price for gasoline plus a decrease of 12 percent in fuel economy will result in a net increase of 25 percent in gasoline expenditures.

Table 65 presents a range of percentage increases in operating costs for representative increases in the price of gasoline and decreases in fuel economy. Percentage increases have been calculated for three sizes of 1972 model automobiles: (1) a full size car with V-8 engine and fuel economy of 13.60

Table 65

Percentage Increases the Costs of Operating  
Cars Equipped With Dual Catalyst Units  
for HC, CO, and NO<sub>x</sub> a, b

Percentage		.00	.06	.12	.18	.24	.30
Increase in the Price of Gasoline	.00	F .05	.06	.07	.09	.11	.13
		C .06	.08	.09	.11	.13	.16
		S .07	.09	.10	.12	.13	.15
	.05	F .06	.07	.08	.10	.12	.14
		C .08	.09	.11	.13	.15	.17
		S .08	.10	.11	.13	.15	.16
	.10	F .07	.08	.09	.11	.13	.15
		C .09	.10	.12	.14	.16	.19
		S .09	.11	.12	.14	.16	.18
	.15	F .08	.09	.11	.12	.14	.17
		C .10	.11	.13	.15	.18	.20
		S .10	.12	.13	.15	.17	.19
	.20	F .09	.10	.12	.13	.16	.18
		C .11	.13	.14	.16	.19	.22
		S .11	.13	.14	.16	.18	.21

a All baseline cost estimates for standard sized (F), compact (C), and subcompact (S) model automobiles were taken from Federal Highway Administration data (U.S. Department of Transportation, 1972)

b Assuming a \$350 increase in the sticker price for the catalytic converter

miles per gallon; (2) a compact car with six cylinder engine and fuel economy of 15.97 miles per gallon; and (3) a subcompact with four cylinder engine and fuel economy of 21.43 miles per gallon.

These estimates include increases in new car prices of \$350 for dual-catalyst emissions control systems and the fuel costs for 50,000 miles of driving. The initial cost of the emissions control system does not vary with the size of the car. Additional costs for maintenance and replacement of the pollution control system have not been included.

These estimates indicate that the relative differences in the costs of purchasing and operating full size, compact, or subcompact cars equipped with emissions control systems are not very great. Furthermore, where there are differences they do not favor the purchase of compact or subcompact cars with better fuel economy. A smaller initial cost for control devices would, of course, have produced smaller differences between full-sized and subcompact cars.

To conclude, there are no incentives in the present strategy for controlling automobile air pollution to encourage consumers to purchase the smaller cars which achieve better fuel economy. The operating cost differentials, which in this case include increased fuel consumption and increases in the price of gasoline, between full-sized, compact, and

subcompact model automobiles do not appear to be large enough to encourage a massive consumer switch to the smaller cars. Given the present consumer tastes for larger cars, EPA's strategy for emissions control will have little or no effect on new car buying patterns.

### 1.6 Recommendations

The Committee on Motor Vehicle Emissions (CMVE) has begun a thorough reexamination of the 1976 nitrogen oxide standard that was established in the 1970 Clean Air Act. The Committee is reassessing its premises, underlying assumptions, the goals that were set and the interplay between the other two pollutants specifically named in the Act. CMVE believes that this reexamination will be valuable in relating motor vehicle emissions control to other issues, for example, energy conservation, which are relevant to national environmental policy.

A reexamination of this kind should also make an assessment of the assumptions and interplay between emissions standards, fuels, fuel additives, and the combustion products of fuel additives. The 1970 Amendments to the Clean Air Act implicitly assume that fuels and fuel additives play a subsidiary role in automobile engine and emissions control tech-



nology. In the design of effective and efficient policies for automotive emissions control, the importance of fuels and fuel additives should be accorded equal standing along with engine and emissions control technology.

Finally, part of the reexamination should include a comprehensive benefit-cost analysis of alternative levels of emissions standards and alternative techniques for emissions control. On the benefits side the analysis should include estimates of:

- (1) the reduction in the risks of adverse physiological effects of automotive emissions of hydrocarbons, carbon monoxide and nitrogen oxides on human health, animals, and crops.
- (2) the reduction in the risks of adverse physiological effects of automotive emissions of lead on human health, animals, and crops.
- (3) the reduction in the risks of adverse physical and other detrimental effects of automotive pollution on property and on environmental aesthetics.

On the costs side the analysis should include estimates of:

- (1) the costs of alternative technical options for controlling emissions.
- (2) the energy impacts of alternative technical



options for controlling emissions. (These estimates should be developed for several different patterns of energy supply and demand).

## Appendix A

Summary of Exhaust Emission Standards  
(All Values Shown Are in Grams/Mile)

	HC	CO	NO <sub>x</sub>
Uncontrolled (pre-1968 vehicles) <u>a</u>	8.7	87	3.1
1973/74 Federal Standards <u>b</u>	3.4	39	3.0
1973/74 Federal Standards Converted to the 1975 FTP	3.0	28	3.1
1974 California Standards <u>b</u>	3.2	39	2.0
1974 California Standards Converted to the 1975 FTP	2.8	28	2.0
1975 Federal Interim Standards <u>a</u> , <u>d</u>	1.5	15.0	3.1
1975 California Standards <u>a</u> , <u>d</u>	0.9	9.0	2.0
1976 Federal Standards <u>a</u> , <u>e</u>	0.41	3.4	2.0
1977 Federal Standards <u>a</u> , <u>e</u>	0.41	3.4	0.4

a Using the 1975 Federal Test Procedure (1975 FTP)

b Using the 1972 Federal Test Procedure (1972 FTP)

c Can only be changed by Act of Congress

d On April 11, 1973 EPA Administrator, William Ruckelshaus granted the automobile industry's application for a one-year suspension of the 1975 motor vehicle emission standards. Since the Clean Air Act requires that interim standards be set if a suspension is granted, in his decision Ruckelshaus promulgated two sets of relatively stringent interim standards; one set for the state of California and one for the rest of the U.S.

In May, 1972, Ruckelshaus had refused the automaker's request for a one-year suspension of the 1975 standards. This decision was appealed and in February 1973 the U.S. Court of Appeals ordered EPA to hold more hearings on the 1975 deadline.

e On July 30, 1973, Administrator, Robert Fri ordered a one-year suspension in the 1976 nitrogen dioxide standard. Fri also established an interim standard for NO<sub>x</sub> emissions.

## Section B. Risk-Benefit Analysis and the Economics of Heavy Metals Control\*

In the past few years a good deal of research has been directed toward achieving an understanding of the characterization, movement, and effects of heavy metals in the environment. Research has also been directed toward the equally important objective of explaining the technical and economic reasons why our economic system utilizes large quantities of heavy metals. Information from both types of research is essential for the design and implementation of efficient strategies for reducing the hazards of heavy metals in the environment. Decision makers must consider the tradeoffs between the economic benefits and the environmental risks of utilizing heavy metals. The purpose of this presentation is to define a framework for benefit-risk decision making for the control of heavy metals.

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\* This section will be published in Peter A. Krenkel (ed.) Proceedings of the International Conference on Heavy Metals in the Aquatic Environment, New York: Pergamon Press, forthcoming.

Heavy metals impart economic benefits to virtually every kind of economic activity. The advanced technology of our mass production economy is highly dependent on the physical and chemical properties of these materials. Each year American industry demands large quantities of copper, zinc, lead, chromium, and nickel, and lesser amounts of beryllium, cadmium, and mercury. As Table 66 indicates, industry has steadily increased its utilization of these and several other metals with known toxic properties in the post war period.

The kinds of economic benefits which stem from the use of heavy metals are as diverse as their physical and chemical properties. For example, arsenic and mercury compounds have been used for their toxic capabilities in pesticides and fungicides; zinc galvanizing and cadmium plating are employed for their materials-saving properties; and lead antiknocks are used for their energy-saving benefits.

The intensive rate of utilization of heavy metals also results directly in the generation of large quantities of waste materials which contain heavy metals and heavy metal compounds. During production activities heavy metal inputs are partly converted into final goods which may contain heavy metals and heavy metal waste materials. Once the services of final goods have been depleted their material contents also become wastes. Consequently, after the economic

TABLE 66

ESTIMATED U.S. CONSUMPTION OF SELECTED METALS,  
1950, 1969, 1970, and 1971<sup>1</sup>

METAL	TOTAL ESTIMATED CONSUMPTION <sup>2</sup> (in tons)				ANNUAL RATE OF INCREASE: 1950-1969
	1950	1969	1970	1971	
1. Arsenic (AS <sub>2</sub> O <sub>3</sub> )	32,104	18,170	18,763	16,406	-2.9
2. Barium (barite)	786,131	1,604,742	1,408,626	1,355,397	3.6
3. Beryllium (beryl)	3,007	8,483	9,496	10,373	5.3
4. Cadmium	4,773	7,531	4,532	5,416	2.3
5. Chromium	980,369	1,411,000	1,403,000	1,093,000	1.8
6. Copper	1,424,434	2,142,218	2,043,303	2,019,507	2.1
7. Lead	1,237,981	1,389,358	1,360,552	1,431,514	0.6
8. Manganese Ore	1,650,429	2,181,333	2,363,937	2,155,454	1.4
9. Mercury	1,870	2,940	2,337	1,994	2.3
10. Molybdenum	13,015	25,811	22,669	20,475	3.5
11. Nickel	98,904	141,737	155,719	128,816	1.8
12. Selenium	546	988	755	529	3.0
13. Vanadium	NA	6,154	5,134	4,802	---
14. Zinc	967,134	1,814,167	1,571,596	1,650,585	3.2

<sup>1</sup>Source: Reference (U. S. Department of Interior b)

<sup>2</sup>Includes stocks released to the open market by the federal government and imports; does not include exports.



benefits of utilizing heavy metals have been realized, their material substance remains and must be either recycled or discharged into the environment.

This conclusion is an obvious reflection of the basic principle of the conservation of matter. Economists have recently integrated the materials balance approach into their analysis of environmental problems (Kneese, A.V., 1970). This approach has economic validity as well as scientific validity in understanding the problems of controlling heavy metals.

Because of their toxic properties the direct discharge of heavy metal wastes into the environment creates a risk of biological damage. The term risk refers specifically to the probability, which may be very small, of damage to living organisms.

Heavy metal waste streams may be treated in order to reduce the risk of damages in the environment. But because it is impossible to ultimately eliminate heavy metals, efforts to reduce the risks of damage in one area of the environment may merely transfer them to another. For example, the removal of heavy metals from industrial waste water discharges may ultimately create a land disposal problem for solid wastes containing heavy metals.

Because of their persistence in the environment, heavy



metals may accumulate in environmental sinks such as the soil or concentrate within the components of the food chain. Again because of their toxicity, any buildup of heavy metals within any component of the environment may pose a threat to man and to other forms of life. These facts are indicative of the risks of using the natural environment as a place of disposal for wastes containing heavy metals.

What do economists mean by the benefits of utilizing heavy metals? A basic assumption of economics states that the benefits of any product are evaluated in terms of the product's ability to satisfy an individual consumer's desires. The consumer expresses his willingness to purchase goods and services in the market place, and he makes those purchases which maximize his level of satisfaction subject to his income and to market prices. In other words the consumer's level of expenditure for each particular product provides a measure of the product's benefits; the benefits of a product are determined at the point of final consumption.

Because consumers generally do not make direct use of heavy metals, the above principle cannot be readily applied. Although the presence of a heavy metal may be essential for the performance of a product, the heavy metal does not provide the motivation for buying the product. Take the storage battery or leaded gasoline, for example. Therefore an

alternative means other than consumer satisfaction must be established for measuring the benefits of heavy metals.

For the most part heavy metals enter as intermediate inputs into the production of final goods and services that consumers enjoy. The value-in-use of any input, including heavy metals, can be measured in terms of the output it generates during the various stages of production. This is the concept of productivity. In practice it is virtually impossible to isolate the productivity of one single input because several inputs are usually combined during the production process.

In addition to productivity producers also select a combination of inputs on the basis of cost. Producers will make additional purchases of resource inputs as long as the cost of an additional unit of input is less than the value of the additional services it provides.

If the implementation of an anti-pollution control forces a producer to eliminate or to reduce the use of a particular input, for example, a heavy metal pesticide, then the producer must substitute an alternative input, such as an organic pesticide, in order to accomplish the same end. Any increase in cost for the substitute input represents a net replacement cost of not being able to use the original input. If no substitute inputs are available, then the

market value of any decline in production represents the foregone economic benefits of not being able to use the original input. The concept of net replacement cost or the concept of foregone economic benefit provides a useful means of measuring the economic benefits-in-use of heavy metals. The USEPA has used this measure in at least one instance in measuring the economic impacts of removing lead additives from gasoline (Bonner and Moore Associates, Inc., 1971).

What do we mean by the risks of heavy metal pollution? A recent colloquium on benefit-risk decision making grouped risks into three categories (National Academy of Engineering, 1972). These are:

1. Risks determined by individual option: This category included risks that are taken voluntarily, sports, smoking, flying in a private plane. Everyone has a propensity for taking risks in order to achieve benefits that outweigh any perceived hazards.
2. Risks determined by individual option but limited by social action: This category includes risk-benefit analyses that are made by individuals subject to limitations imposed by society. An example is the use of drugs in medicine.

3. Risks determined by social action decisions: Certain kinds of hazards are pervasive; they may affect large segments of the population. In addition the individual usually has no immediate control over the casual agent. The hazards are public "bads", and they are subject to government control.

Environmental pollution from heavy metals clearly falls into the third category of risk.

We may illustrate the risks and benefits associated with the use of heavy metals with the environmental-economic systems diagram in Figure 10. The following paragraphs deal with lead as an example for illustrating what the diagram means.

Lead is one of the most intensively used industrial metals, and, as a direct consequence of its widespread use, lead and lead compounds are discharged into the environment in extremely large quantities. In 1971 alone industries in the United States utilized over 1.43 million tons of lead (U.S. Department of Interior b); lead ranks fifth, behind iron, copper, aluminum, and zinc, in terms of total tonnage consumed. This widespread use can be attributed to the versatile chemical and physical properties of lead and to the favorable economic factors involved with obtaining and processing the metal in the mineral state.



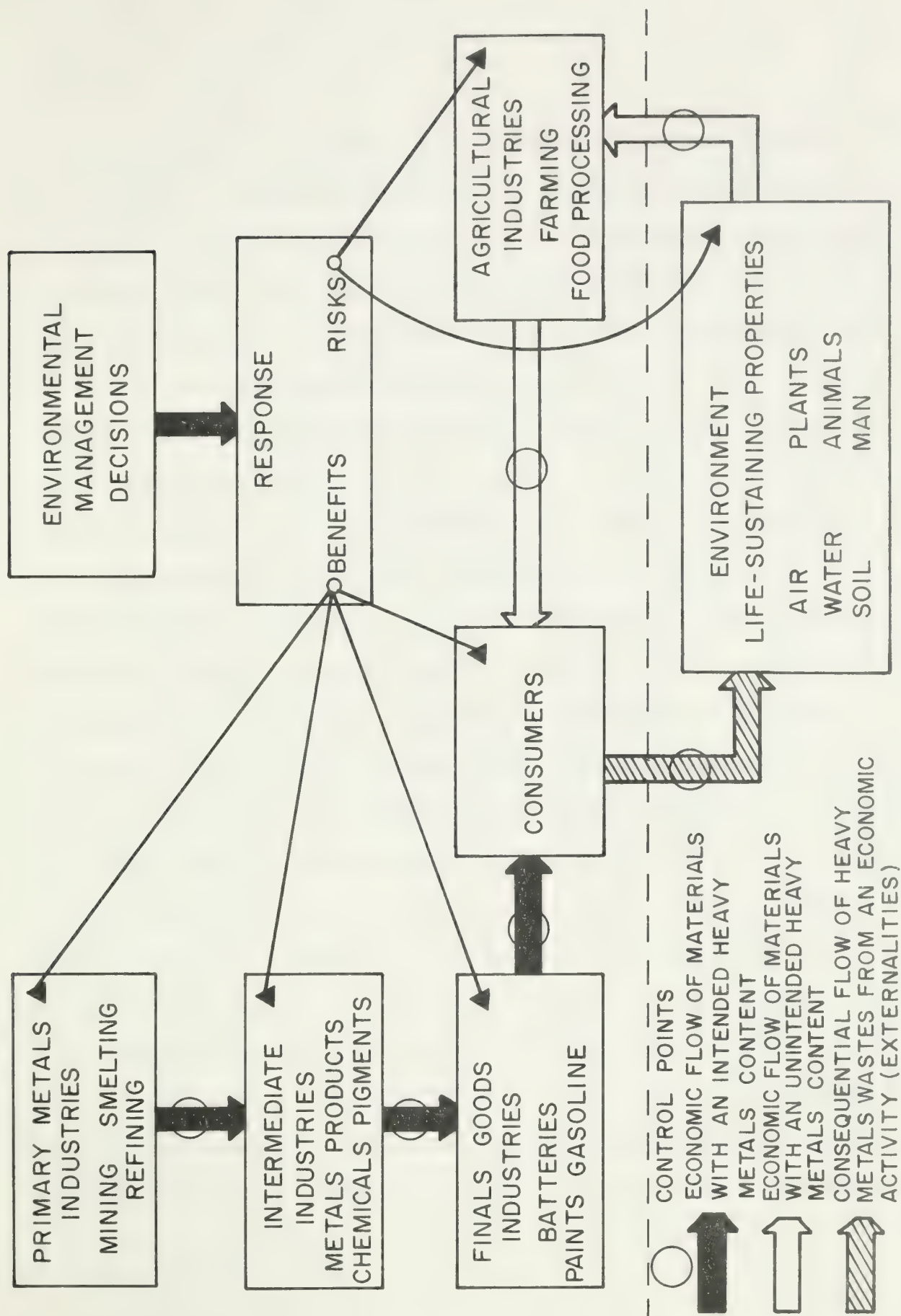


FIGURE 11C. ECONOMIC-ENVIRONMENTAL SYSTEM FOR HEAVY METALS

Lead is the heaviest and the softest of the common metals, it is abnormally resistant to chemical corrosion, and it alloys very easily with several other metals. Lead also has low melting and high boiling points, and it has very useful energy absorption and transmission qualities. The usefulness of lead in the fabrication or composition of any product is, to a large extent, a function of one or more of these characteristics.

The high frequency of occurrence of economically viable lead ore deposits and the relative geographic convenience of these sources has facilitated meeting industrial demands for lead metal at a very low cost. For example, the large galena ore deposits in southeastern Missouri have made that region one of the most productive lead mining regions in the world. In 1971 the Missouri lead belt, which is conveniently located for transporting lead to markets, accounted for 74 percent of the total domestic lead in ore (U.S. Department of Interior b).

The combination of these two factors--a large number of desirable properties and the relatively low costs of extraction--have encouraged intensive use of the metal. In the absence of any regulations that prohibit the manufacture and distribution of products that contain lead, the relatively low price for this material will continue to be an incentive for its widespread use.



Figure 110 illustrates the interindustry production and utilization of lead. Lead production begins, of course, at the mine. Mined ore is then crushed and dressed in a number of operations to effect mineral separation. The resultant lead concentrate is then smelted and refined into lead metal of varying degrees of purity.

In 1971 domestic mine production of recoverable lead contributed 88 percent of the total U.S. supply of primary metal. Imported ores, concentrates, and pig-lead accounted for the remainder. Primary lead accounted for about 60 percent and secondary or recycled lead output represented about 40 percent of the total U.S. market supply. The total domestic supply of lead, primary, secondary, and imports, amounted to 1.46 million tons (U.S. Department of Interior b).

As Figure 110 illustrates primary and secondary lead output is then sold to intermediate industries for fabrication and processing into other commodities. In other words lead is an intermediate commodity that becomes an ingredient in many of the final goods that eventually reach the consumer.

The major demands for products that contain lead are related to uses in transportation. For example, the storage battery and gasoline additives industries absorbed approximately 45 and 20 percent, respectively, of industry's total

consumption of lead in 1971. The data in Table 67 provide a more detailed view of interindustry utilization of lead during the past decade. In this period the amount of lead utilized in pigments and metals products has declined while the quantities used in ammunition, batteries and gasoline additives have increased rapidly. The 10-year average annual rate of growth of lead used for gasoline additives is twice as high as the growth rate for all lead consumption.

It is within the interindustry network that the benefits of lead and lead compounds are realized. The patterns of demand and supply reflect industries' selection of materials according to their prices and their properties. Tetraethyl lead (TEL), for example, is used as an inexpensive substitute for higher octane, more expensive blending components in the production of gasoline. The addition of a few cubic centimeters of TEL enables refiners to produce high octane motor fuels with less crude oil and with less severe processing than would be required in the production of unleaded gasolines.

The flow of lead emissions that enter the environment is integrally related to the economies of lead production and utilization in the following manner. Lead enters the ecosystem as a constituent of various solid, liquid, and gaseous waste products. These wastes are discharged as a direct con-

TABLE 67

## SELECTED TRENDS IN THE LARGEST CATEGORIES OF

## INDUSTRY'S UTILIZATION OF LEAD 1963-1972

Manufacturing Category	IN PERCENTAGES OF TOTAL LEAD CONSUMED <sup>1</sup>										Average Annual Rate of Growth
	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	
Storage Battery Grids, Pastes, and Oxides	37.8	35.8	36.7	35.7	37.0	38.6	41.9	43.6	47.5	45.5	4.0
Gasoline Additives	16.6	17.0	18.1	18.6	19.6	19.7	19.5	20.5	18.4	19.5	4.6
Pigments	8.5	8.6	8.8	9.1	8.2	8.3	7.3	7.2	5.7	6.3	-1.3
Ammunition	4.3	4.7	4.6	5.9	6.3	6.2	5.7	5.4	6.1	5.9	5.3
Other Metal Products	29.7	30.6	28.4	27.3	25.8	24.1	22.5	20.5	19.5	20.3	-3.4
Miscellaneous	3.1	3.3	3.4	3.4	3.1	3.1	3.1	2.8	2.8	2.3	-0.3
Total Lead	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	2.3

<sup>1</sup>Source: Reference ( U.S. Department of Interior b)<sup>2</sup>Preliminary

sequence of using lead or products that contain lead in certain economic--transportation, production, consumption-activities. The amount of waste that is discharged is a direct function of the level of economic activity. For example, the combustion of leaded gasoline which is the primary fuel for our land transportation system accounts for approximately 96-98 percent of the airborne emissions of lead (Engel, R. E., et al., 1971).

Any environmental management decision that is directed toward reducing the flow of lead that is currently entering the environment will obviously reverberate back through the lead and lead products industries and possibly through several other supplying industries such as mining equipment, construction, and transportation as well. The extent and intensity of these effects may be quite diverse and will depend on several factors including the size of the reduction, its timing, regional concentration of the affected industry, economic conditions in the industry, and the overall economic importance of the restricted product.

Consider the energy-economic implications of USEPA's proposals for eliminating the use of lead additives in gasoline. The tetraethyl lead industry absorbs nearly 20 percent of the total annual industrial consumption of lead in the United

States. This is primary lead for the most part and therefore, a decline in the use of lead additives will bring immediate losses in income and employment to the primary lead mining and smelting and tetraethyl lead industries. Although EPA has proposed a phased-reduction plan that will take several years to complete, the lead mining and smelting industries are highly concentrated in Missouri, Utah, and Idaho, and the economic losses to those areas are likely to be severe. The fact that a large part of the lead industry in Missouri consists of modern, low-cost operations, however, may enable some mining and smelting companies to ride-out cutbacks in domestic consumption by expanding sales in foreign markets.

As indicated above the addition of tetraethyl lead results in energy-saving benefits in the production of high octane gasolines. High octane gasolines (94-100 RON) are necessary for the efficient operation of engines with compression ratios in the 9:1 to 10:1 range. All things being equal, these engines achieve better fuel economy than engines with lower compression ratios.

EPA's overall strategy for controlling automobile air pollution will, in all likelihood, require the use of catalytic emissions control devices. Lead emissions from the combustion of lead gasoline have a deleterious effect



on the operation of these devices. Consequently, in 1971 Detroit began producing automobiles with lower compression ratios that run on lower octane unleaded gasoline in preparation for the introduction of the catalytic converters in 1975 and 1976.

The compression ratio drop in the post-1970 automobiles has had an adverse effect on fuel economy. The addition of the catalytic emissions control systems will also produce additional adverse effects. In a study that was completed for EPA, Bonner and Moore Associates, estimated the federal government's strategy for controlling automobile emissions will result in an increase in the demand for gasoline of 9.2 percent or over 10 billion gallons per year by 1980 (Bonner and Moore Associates, Inc., 1971).

To conclude the example, tetraethyl lead provides rather significant economic benefits which in view of the present energy crisis, may be too valuable to forego. At the same time the risks of allowing increasing amounts of lead to enter the environment warrant some kind of controls on the use of tetraethyl lead. The problem that decision makers must solve concerns where between the extreme positions of total restriction and no restriction on the use of lead in gasoline--to place the level of control.



As a first step in making this kind of decision, decision makers must have an analytical framework for organizing the components of the problem they want to resolve. In this regard benefit-risk analysis provides a practical method for comparing the relevant economic benefits with the environmental risks of using heavy metals.

As the name implies, benefit-risk analysis is somewhat akin to benefit-cost analysis; both forms of analysis provide a systematic method for assembling information about the prospective benefits and costs of a government program decision. The name "benefit-risk" analysis may be somewhat of a misnomer because "benefit" refers to the foregone benefits or the costs of not being allowed to use a particular material. "Cost-risk" analysis may be a more appropriate term to use.

As Figure 111 illustrates a benefit-cost ratio is the ratio of the discounted stream of benefits to the discounted stream of costs that accrue to the public from a particular government program. A benefit-risk ratio is the ratio of the discounted stream of economic benefits gained (lost) to the discounted stream of the expected values of the risks of environmental damages which increase (decrease) with the benefits of using (not using) a heavy metal. By discounted stream we mean the present value of prospective benefits and expected

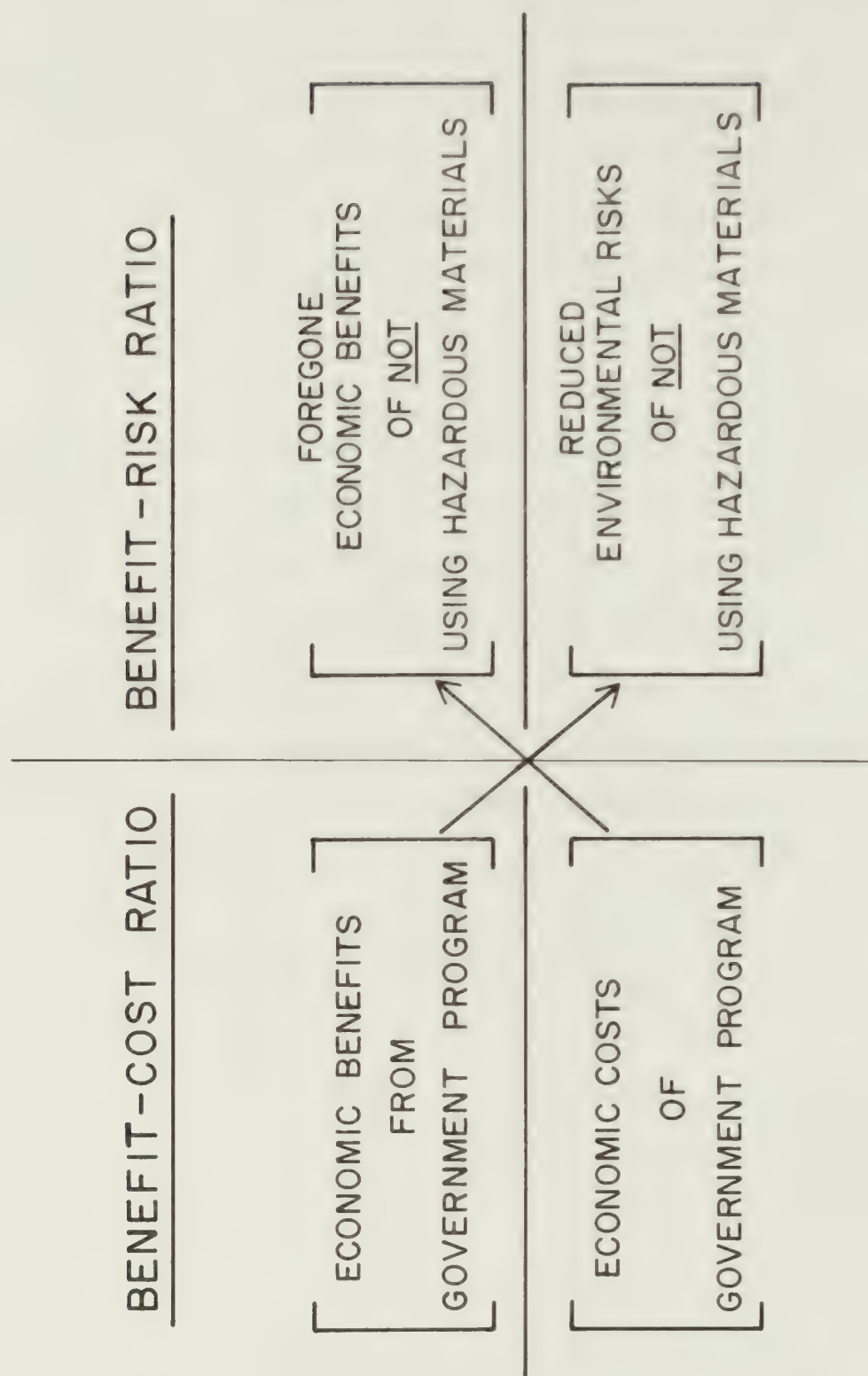


Figure 111 Benefit-Cost Ratio Versus Benefit-Risk Ratio

values of the risks of environmental damage. The present value of benefits, for example, is expressed as

$$(1) \quad P.V. = \sum_j \frac{B_j}{(1+r)^j}$$

where  $B_j$  is the dollar value of benefits that accrue in the  $j^{\text{th}}$  time period and  $r$  is the appropriate rate for discounting.

The benefits of using a heavy metal can be estimated directly using price-quantity information and either the net replacement cost approach or the foregone economic benefits approach discussed above. The expected value of the risk of environmental damage from the use of heavy metals, however, can only be estimated indirectly from monitoring information and from data on the health, plant, and animal effects of ambient concentrations of heavy metals in the environment.

Benefit cost analysis has long been used to evaluate public expenditure programs of various kinds (Prest, A.R., and R. Turvey, 1965). The most notable examples include river basin developments, urban renewal projects, and public health programs. In addition benefit-cost analysis is a useful tool for evaluating the economic consequences of a regulatory decision (Schmid, A. Allen, 1969). In both of these situations, however, the benefits and costs are esti-

mated with reasonable certainty. If there is considerable uncertainty in quantifying costs and benefits, an ad hoc probability factor may be used to give a range of estimates instead of a single estimate.

For benefit-risk analysis the importance of probability is really the heart of the analysis. The probability that certain events will lead to a specified outcome, i.e., the probability that an ambient environmental concentration of heavy metal will have an effect on an organism, is the basis for assessing risk. The crux of risk-benefit decision making lies in balancing the probabilities of damaging effects to organisms against the reasonably certain economic benefits.

The problem of estimating the improvements in public health that result from a program of disease control is analogous to the problem of estimating the reduction in environmental risks that result from a program of pollution control. In the disease control program the measure of improvement is a function of the reduction in the incidence of a particular disease, and in the pollution control program the measure of improvement is the value of environmental damages that society avoids vis-a-vis the implementation of the control program. A comparison of the measurement of

improvement in public health to the measurement of improvement in environmental conditions will serve to illustrate the fundamental importance of probability in risk-benefit analysis.

The measure of improvement is a function of the difference between a baseline measure of the incidence of disease or environmental damage and the anticipated results of the control measures. The following equation summarizes the measure of benefits for the  $i^{\text{th}}$  segment of the population.

$$(2) \quad M_i [E(Y_i) - E(\hat{Y}_i)] = B_i$$

$E(Y_i)$  is the expected number of illnesses or deaths due to disease in the absence of a disease control program;  $E(\hat{Y}_i)$  is the projected number of illnesses or deaths after the program has been implemented.  $M_i$  is an arbitrary average cost factor for a single illness or death. The conceptual framework for estimating the cost factor  $M_i$  is well established for disease control programs. These costs include two components, (1) the direct costs of medical care and (2) the indirect costs of losses in productivity due to death or illness (Klarman, Herbert E., 1965).

The incidence,  $Y_i$ , of disease is measured directly from data collected by public health authorities. It is important



to note diseases with low incidence rates pose a special disadvantage in terms of lack of data. This is essentially the same "can of worms" that plagues the measurement of health or biological damage due to heavy metals in the environment.

The incidence of damage to the health of the general population due to heavy metals in the environment is not directly observable in the same sense as the occurrence of disease. Many of the effects of an increase in heavy metal pollution are subclinical and therefore go undetected. Some of these effects may be latent and turn up well after the toxic stress is no longer present. Finally the effects of a heavy metal are dependent on concentrations reaching the individual, and these, in turn are dependent on stochastic variables such as the weather conditions and distance from the source of emissions. Because of these stochastic factors the number of occurrences must be estimated using the following kind of probabilistic damage response function (Schwartz, Seymour, 1971).

Equation (3) defines the expected value of a probabilistic response function for specified ambient levels of pollutant.



$$(3) \quad E(x) = \sum_j \sum_i (x_i f(x_i | c_j)) f_c(c_j)$$

In this equation the expected response,  $E(x)$  is the percentage of the population that is affected by various concentrations,  $c_j$ , of pollutant.\*

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\*A set of joint observations on two variables, concentration,  $c$ , and effect,  $x$ , may be organized in the form of a joint frequency distribution,  $f(x,c)$ . For each  $(i,j)$  pair of values  $f(x_i, c_j)$  is the relative frequency with which it occurs in the sample set of observations. If in the joint distribution, one of the variables,  $x_i$ , is conditional on the outcome of the other,  $c_j$ , then the conditional frequency distribution is written as  $f(x|c_j)$ , and  $f(x_i|c_j)$  is the relative frequency  $x$  occurs in the subset of variables  $c_j$ . Because each conditional frequency is the ratio of a joint frequency to the frequency of the conditional variable, we have

$$f(x|c) = f(x,c)/f_c(c)$$

or 
$$f(x|c)f_c(c) = f(x,c).$$

Finally, the expected value,  $E(x)$  of a sample of observations is the mean of the sample. For a conditional frequency distribution the expected value of one variable for a given value of the second is expressed as

$$E(x) = \sum_i x_i f(x_i | c_j)$$

Expected response is a function of the probability,  $f_c(c_j)$ , that ambient concentration,  $c_j$ , will occur at a receptor point and the relative frequency,  $f(x_i|c_j)$ , that a random event,  $x_i$ , occurs in the sample population. The random event in this instance is the percentage of the sample that exhibits a particular biological effect at concentration  $c_j$ . For example,  $f(x_i|c_j)$  is the relative frequency that 10 percent of the sample population will have a blood lead concentration of  $20\mu\text{g}/100\text{cc}$  of blood after being exposed to ambient airborne concentrations of  $1\mu\text{g}/\text{m}^3$  of lead for one month.

The expected number in the  $i^{\text{th}}$  population group affected is obtained by multiplying the size of the  $i^{\text{th}}$  group,  $Y_i$ , by the expected response,  $E(x)$ .

$$(4) \quad E(Y_i) = Y_i \left[ \sum_j \sum_i (x_i f(x_i|c_j) f_c(c_j)) \right]$$

The expected change in the incidence of these damages in the  $i^{\text{th}}$  population group is defined in terms of the difference in the expected number of occurrences of the pollution effect at a baseline or no-control level of pollution and a target level. The expression on the left-hand side of the minus sign in equation (5) is the expected level of damage at the no-control level of pollution, and the expression

on the right is the expected level of damage at the targeted level of heavy metal pollution control. The difference between these two levels is the basis for measuring the benefits of pollution control

$$(5) \quad B_i = M_i \{ Y_i [ \sum_{j=1}^J (x_i f(x_i | c_j) f_c(c_j)) ] - \hat{Y}_i [ \sum_{j=1}^J (\hat{x}_i f(\hat{x}_i | \hat{c}_j) f_c(\hat{c}_j)) ] \}$$

The "capped" terms denote values which must be predicted if the benefit-risk analysis is made ex ante. Predictive simulation models of environmental processes provide the means for predicting changes in ambient concentrations and changes in biological responses for specified changes in the level of heavy metal pollution.

Equation (5) suggests that in order to estimate risk, considerable research is needed to define the following parameters:

1. The probability distribution for ambient concentrations at receptor points.
2. The conditional probability distribution for damage to all receptor population.

Monitoring information can be used to construct the probability distributions for ambient concentrations. The conditional response probability distribution is much more difficult to obtain; these distributions must be constructed

from expensive and time-consuming epidemiological studies.

Further problems involved in constructing this kind of conditional probability transformation arise because the pollutant may not have the same effect on different target groups within the population; the effects of the pollutant may be dependent on factors other than ambient conditions. In addition the occurrence of harmful physiological effects at low levels of exposure may be questionable.

In conclusion risk-benefit analysis may serve as the basis for rational decision making to control heavy metal pollution. A great deal of research will be needed, however, in order to perfect this analytical tool.



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VII. ANALYTICAL LABORATORY

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## VII. Analytical Laboratory

### A. Introduction

During the present reporting period the Environmental Research Analytical Laboratory processed a total of 18,189 results (see Table 69 of the following section) at an annual rate of 15,590 compared to 15,600 for the corresponding period reported in PR2. This was accomplished with a 20% smaller staff. This apparent increase in efficiency has resulted from the combined influences of several factors. First, the laboratory has acquired an extensive repertory of tested, in-place procedures for the determinations most requested by users. It has been possible to process all the sample types encountered this year (with the exception of air filters) by means of reliable procedures which have needed little experimentation. Were it not for this fact the present staff and budgetary restrictions which have reduced research and development to less than 5% of total activity time would have been intolerable to the project. Second, the average tenure of the technical staff has increased from 1.8 years to 2.57 years despite a 40% loss in personnel. This has meant a savings in time and effort due to greater familiarity



with laboratory operations as well as increased professional growth. Third, users and laboratory personnel alike have learned to appreciate mutual needs and requirements more fully. This has resulted in a substantial increase in the number of properly prepared and accurately submitted samples thus reducing the amount of time spent in straightening out communication snarls. Fourth, the smaller number of participating groups has resulted in fewer but larger field or laboratory investigations. This has shifted the emphasis in analyses from short-run, variable sample types to high-run single sample types with a resulting efficiency created by not having to change instrument settings or procedures as frequently. Finally, a much improved method and equipment for electrochemical (ASV) assays has contributed to the increased throughput albeit not as demonstrably as hoped.

Once again the laboratory and its users have experienced the annual phenomena of sample backlog increases and analysis report delays occasioned by the uneven sample submission rates created by immutability of growing season time scales. A combination of circumstances contrived to make the major impact of this years delays fall on the efforts of only a few users.

At root cause is the fact that the laboratory must acquire its staff based on annual averaged work loads while users find it useful to use temporary student help during the growing season. The result is annual verification of the truism that it is easier to acquire samples than to analyze them. The immediate result is that the laboratory is always either under-or overstaffed. The overstaffed situations of late Winter and early Spring have offered the only real opportunity for the laboratory to do the research and methods development necessary to maintain its skills. However, when the averaged annual sample submission exceeds the averaged annual work capacity of the laboratory the resulting backlog stacks up quite quickly and dissipates slowly.

Inspection of Table 69 reveals no particular pattern of sample input-output that might be dealt with in a formal fashion. The simplest explanation for the summer season shortfall is that the annually averaged staff work capacity is simply overwhelmed by high sample input during the growing season resulting in a backlog that is dissipated slowly. A combination of past experience and running input-output figures as in Table provided an early indication of the need to counter the growing



backlog as early as September, 1973. A review of the numbers, types of samples, and requested assays suggested that acquisition of a new AA unit would be effective. The proper purchase procedures were instituted on September 5, but through an extraordinary combination of small delays in processing, missed deadlines, vacations of key purchasing personnel, labor disputes, and truck strikes the total process will have required over 180 days when the unit is finally installed in early March. The probability that such events will cooperate in like fashion again is extremely remote.

General improvements in procedures and methods continue as in the past to be accomplished "on the run". In-process samples of appropriate characteristics are examined in duplicate under the existing procedural conditions as well as the contemplated new condition. Results and experimental statistical design are thus judged by methods which do not require a "true value". A typical experiment would involve a two-way classification with replication and an analysis of variance using mean differences as the fundamental statistic. Statistical analysis of data has been facilitated by the use of the University of Illinois SOUPAC statistical package and the in-house residence of Drs. George Provenzano and Garland Wheeler of the Modeling Group.

A long-standing conflict between laboratories and procedures for assays of heavy metals in samples requiring destruction of organic matter concerns the trade-off decisions of suspected losses of metal in thermal dry ashing compared to hazards, erratic behavior, and high blanks reported for wet ( $\text{HClO}_4$ ) ashing treatments. A partial answer at present applicable only to soils--a non-typical sample type of relatively low organic content--has been obtained from the analysis of a series of samples which had been degraded by dry ashing cycle that is standard procedure in this laboratory (see PR2 and PR3). A randomly selected sub-set and resampled and degraded by 9:1  $\text{HNO}_3$ : $\text{HClO}_4$  wet ashing to dryness followed by takeup in 3M  $\text{HCl}$  so that the procedure differed only in the manner of destruction. Both sets were analyzed by conventional AA practices for Pb and Cd. Results for Cd produced a best fit linear regression line of:  $[\text{Cd}]_{\text{wet}} = 0.025 + [\text{Cd}]_{\text{dry}}$  based on comparisons of 26 samples analyzed for Cd by both procedures. Analysis of variance of the regression line indicates the intercept of 0.025 to be insignificant at the 95% confidence level and the slope insignificantly different from 1.000--the predicted slope for no methods bias. A smaller set of 8 samples assayed for Pb gave the

regression line:  $[\text{Pb}]_{\text{wet}} = 0.049 + [\text{Pb}]_{\text{dry}}$ . Variance analysis in this case showed the intercept to be significant while the slope was again insignificant from unity. The differences in significance between the two intercept or "blank" values for Pb and Cd have been noted independently several times in this laboratory: reagents tend to have measurable amounts of Pb but not Cd. Additional work in this area involving samples of higher organic content is contemplated in the future. The present results are somewhat at variance with literature reports (see Gorsuch, Destruction of Organic Matter) wherein serious losses of Cd are reported from dry ashing at temperature slightly in excess ( $500^{\circ}\text{C}$  as compared to our  $490^{\circ}\text{C}$ ) of the furnace temperatures in use here. It is conceivable that the losses are proportional to the amounts of combustible materials present in some fashion such that soils are not good general examples. However, it should be noted that this represents the third such directed experiment carried out in this laboratory to test reputed thermal ashing losses which has failed to substantiate such claims.

A similar experiment comparing AA and ASV assays for 39 representative samples showed no methods bias between the two albeit with lesser certainty due to the extreme

dilution factors necessary to adjust the same solutions to the ppb range for ASV measurements.

A set of 171 ASV results obtained from Stream water samples which had been assayed for both Pb and Cd were subjected to SOUPAC statistical analysis to test for any correlation between Pb and Cd, contents. Results show no apparent relation between the two.

The foregoing examples are cited as representative of the kind of investigation available to the laboratory in its efforts to remain current and effective: ad hoc small-scale experimentation based on samples in process of analysis in order to establish or test a specific question or examine an unusual behavior. This is also a minimal research and development program for an operation centrally important to a large project. We estimate that the staff has been able to devote less than 5% of its time to R&D work. With the exception of a minimum program in emission spectroscopy all such efforts have been obtained from and devoted to improving ongoing analyses. The emission spectroscopy work would stand in like manner were it not for the fact that this mode of analysis is not currently used for routine samples in this laboratory.



### Analytical Exchanges and Other Interactions

The laboratory participated in an intercomparison study of analytical results for trace metals in water standard samples distributed by the International Atomic Energy Agency at Vienna. The analytical results obtained according to existing procedures have been reported; and an evaluation of the results of the participating laboratories is expected in approximately three months.

An exchange of analytical results between this Laboratory and the Illinois Geological Survey for the analysis of cadmium in coal-ash samples showed no significant bias (less than 4%) between the two laboratories.

The laboratory provided a referee analysis for lead in Lake Michigan sediment for the Illinois State Geological Survey. The analytical value obtained by 3N HCl leaching of the ashed sediment followed by atomic absorption measurement was not statistically different from the official USGS method involving complete mineralogical decomposition of the sample.

Studies of Dr. John Hassett in soil-metal interactions required trace metal analysis of narrow discrete zones of a soil packed column. This laboratory provided a design, and constructed columns with an integral extrusion device

that provides a convenient means for precise sampling of 4-mm wide zones along the height of the column.

## B. Research and Development

### 1) Atomic Absorption

The focus of efforts in this area has been on the optimization of methods, refinement of the measurement processes, application of computer programs to data processing, and improvements in micro-sample techniques.

Atomic absorption and emission methods have been applied to analysis for an increasing number of elements including As, Sb, Be, Ca, Cd, Pb, Mg, Mn, Tl, and Zn in a wide variety of materials.

Methods have been developed and procedures put into routine use for the determination of lead and other heavy metals in glass-fiber and membrane type air filters, and in street and house-dust samples relating to research support in urban-compartment studies.

The process of standard addition to determine the matrix factor has been refined by the addition of a second generation computer program for both Delves Cup and solution aspiration methods. In addition to the matrix factor, the computer program provides the regression coefficient of the line, a precision estimate, and the limit of detection. The computer printout flags output data that fall outside of



established precision limits.

A preliminary investigation was made of the gaseous hydride method for metals which are capable of forming a volatile hydride (As, Sb, Se, Ge, S, Hg metal) using Sb as the test element and the requisite glassware on loan from the Illinois Regional EPA Laboratory. Preliminary results, using the published methods, were marginally reproducible but recoveries were considerably less than quantitative. Initial observations are that the yield per repetitive trial on a single sample can be as low as 50% and that yield is a function of pH. This previously unreported phenomenon will be investigated.

#### AA Micro Sampling Systems

The Delves Micro-Sample AA technique is invaluable for trace analysis where sample size is limited, but requires a high degree of operator skills to obtain acceptable results. Consequently, a majority of laboratories engaged in trace metal analysis of semi-micro samples generally avoid the Delves technique in favor of the graphite (Massmann) furnace or graphite-rod technique.

Since the Delves Micro-Sample technique had been in use in this laboratory with better than average success, and since the graphite furnace was not available to us at

that time, an investigation was made with the objective of making the Delves method less demanding of analyst skills without degrading analytical performance. System variables studied were absorption tube and aperture geometry, cup position with respect to the absorption tube and the flame, cup-retainer design with respect to heat transfer and geometric stability, and burner head geometry.

Changes made to date have included enlarging the absorption tube diameter and aperture to relax the alignment tolerances of the system elements, and reworking the cup retainer and slide assembly to provide more reproducible system geometry. As a result of these changes, the operating convenience of the system has been considerably improved, and set-up time has been reduced. Analytical performance remains the same with respect to precision and has been improved in sensitivity.

A second Perkin Elmer Delves Sampling System was adapted to the JACO 810 instrument by means of a simple mounting bracket which is less cumbersome, is easier to install and remove, and provides greater dimensional stability than the original fabrications by JACO or Perkin Elmer. The time consuming set-up and optical alignment manipulations have been significantly reduced by the use of optical alignment jigs and targets. Other mechanical modifications

were made to stabilize the geometry of the quartz absorption tube with respect to the flame and optical axis of the spectrometer.

Routine operation of the Delves system was hampered by repeated metallurgical failure of the metal loop which positions the sample cups in the air-acetylene flame. A spectrographic examination identified the loop material to be a nickel-chromium steel. Consultation with the U. of I. Department of Metallurgy suggested the use of Inconel rather than stainless steel. A loop was made of Inconel and has maintained its integrity over a period of approximately six hundred analytical measurements before replacement, compared to less than one hundred for the stainless steel loop.

Procedures have been optimized for the routine determination of lead in blood samples by the Delves technique. A summary of analytical conditions is given in Table 68.

The dual-channel dual-monochromator functions of the JACO 810 have been invaluable in differentiating the non-selective absorbing so-called "smoke" from the lead peak. Since the "smoke" peak height is less reproducible and is sometimes greater than the lead signal, correction for this non-selective absorbance must be made for every lead measurement. The ability of the 810 in the "A-B" mode to automatically accomplish this makes the precision and accuracy of the

TABLE 68

Analytical Conditions for the Determination of Lead in Blood  
by Delves-Cup Atomic Absorption Spectrophotometry

---

Sample Preparation

200ul blood samples measured into 5-ml beakers\*

Wet ashed with 1:9  $\text{HClO}_4$ : $\text{HNO}_3$ \*\* and residue dissolved in 1-ml 3N  $\text{HCl}$ \*\*. Triplicate 50ul aliquots measured into pretreated Delves Cups and stored in sealed containers as described in text.

\*sampled at research site. See Atomic Absorption in

\*\*redistilled or premium purity reagents

Instrumental Conditions

AA Spectrophotometer: JACO Model 810 Dual-Channel  
Double Beam

Wavelength Settings:

Channel A: 283.3nm (Pb absorption)

Channel B: 287.3nm (Background absorption)

Absorption Cell:

Perkin-Elmer/JACO modified as described in text.  
Nickel cups.

Acetylene: Air @7:37 cfh through single-slot Ti-head burner. Bottom of Delves Cup positioned 1mm above flame inner cone. Cup rim tangent to outer surface of quartz absorption tube modified as described in text.

Absorption Measurements

Preparatory to flaming, loaded cups heated @ 140°C on hot plate.

Background-corrected Pb absorption peaks (Ch A-ChB) recorded on two-pen strip chart.

Calibration and Data Processing

Peak-height measurements on samples and standard additions of 10, 20, and 30 ng. One standard-addition cycle for each group of twelve samples. Samples and standard additions are run in triplicate.

Computations of absorption data and printout of analytical results by computer program DELVE II

ENVIRONMENTAL ANALYTICAL LABORATORY

Table 69

Input-Output for the Period November 1972 - December 1973

<u>Dates</u>	<u>Samples</u>	<u>Input</u>	<u>Output</u>	
		<u>Analyses Requested</u>	<u>Total Analyses Reported</u>	<u>Micro Methods* (Delves Cup)</u>
1972				
Nov.	750	841	698	
Dec.	974	1,306	1,169	30
1973				
Jan.	1,582	1,760	1,452	
Feb.	1,153	1,473	1,468	89
March	2,136	2,291	1,410	99
April	1,140	1,188	1,263	56
May	1,402	1,733	1,840	128
June	1,763	2,782	1,197	86
July	1,729	1,751	1,375	45
Aug.	1,437	1,613	1,173	46
Sept.	782	958	1,083	165
Oct.	1,660	1,916	2,233	24
Nov.	1,206	1,489	1,472	32
Dec.	<u>680</u>	<u>791</u>	<u>356</u>	<u>      </u>
<u>Totals</u>				
(Nov. 72- Dec. 73 )	18,394	21,892	18,189	800
(Nov. 71- Dec. 72)	Figures Not Available		11,755	0

\*Included in Total Analyses Reported



lead signal in real life samples comparable to aqueous standards.

The very small absolute amounts of lead (0.5-20ng) measured in sample aliquots in the Delves method require more than ordinary precautions to minimize contamination of samples during preparation and absorption measurements. A factorial experiment to investigate the relative probability of lead contamination during each procedural step demonstrated a relatively high frequency (approximately 30%) of contamination in amounts corresponding to twice the basal blood-lead levels from 15-minute exposures of sample cups to ambient atmospheres.

The use of nitrogen-pressurized enclosures for sample preparation has reduced the occurrences of incidental contamination from 30% to a negligible fraction of samples.

The routine analysis of blood samples from animal studies has been made more efficient and less susceptible to contamination by revising the sample collection and preparation procedure. In the revised procedure, measured analytical samples of blood (~200  $\mu$ l) are taken at the experimental site and placed in precleaned 5 ml beakers provided by the laboratory in compartmented sealable containers holding 18 sample beakers each. After sample collection, the containers



are sealed and sent to the Analytical Laboratory. The potential contamination from intermediate sample containers, anti-clotting reagent and associated handling are thus eliminated.

A current investigation is concerned with some anomalies of the Delves technique with respect to the response of lead. In the determination of lead in animal and plant tissue, the strip-chart trace frequently shows two separate peaks instead of the single idealized peak. Since the analytical measurement of absorption is made on the basis of peak height, the presence of two partially resolved peaks presented a problem of identity as well as measurement. The early works of Delves and others, concerned with lead in blood, (1,2) ascribed the first evolved peak to smoke and other combustible materials, and the second to lead. A later work by Cernik, 1973 attributed the first peak to molecular lead species and the second to atomic lead species, and showed how the first peak could be eliminated by pre-heating the Delves cup to 425°C before insertion into the flame.

Experience in this laboratory has shown that the so-called "smoke" absorption peak appears also from samples containing no combustible material, as well as when the output signals are corrected for non-specific absorption. (Figure 112)

Pb 283.3nm — Bkg.

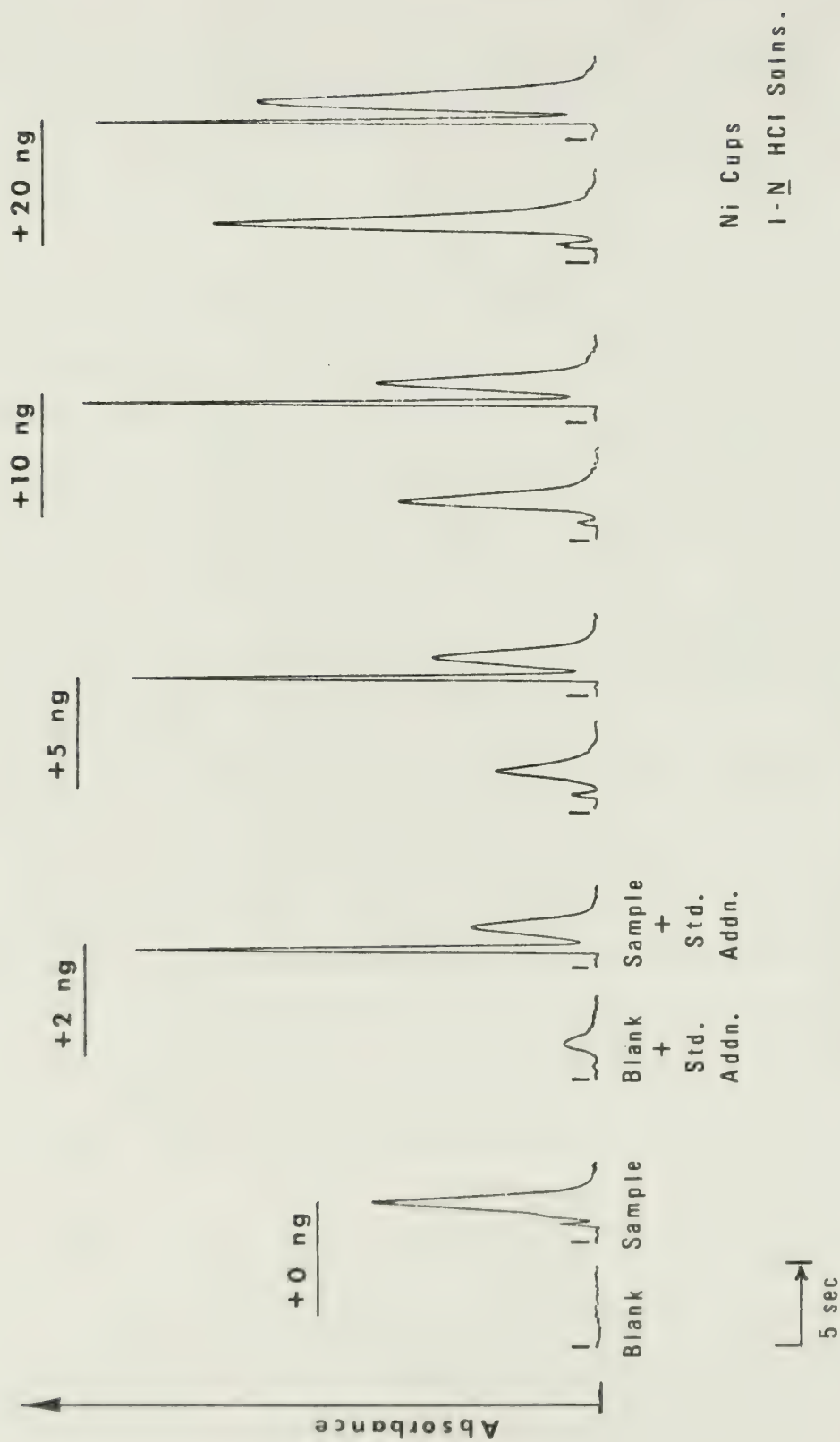


Figure 112

Absorbance vs. Time Profiles of Head in Animal Tissue by the Delves-Cup Method

To test the hypothesis of Cernik that the first peak is due to molecular lead species (a  $\text{PbCl}_2$  band system exists in the UV with band heads at  $2827\overset{\circ}{\text{\AA}}$  and  $2833\overset{\circ}{\text{\AA}}$ ), (4) strip charts of background corrected lead evolution from Delves cup preparations were obtained at  $\text{Pb } 2833\overset{\circ}{\text{\AA}}$  and also at  $\text{Pb } 2170\overset{\circ}{\text{\AA}}$ --the latter wavelength being free of molecular spectral bands. The resultant strip charts showed similar double peaks at both  $\text{Pb } 2833\overset{\circ}{\text{\AA}}$  and  $\text{Pb } 2170\overset{\circ}{\text{\AA}}$ , thereby not supporting Cernik's hypothesis that molecular absorption was responsible for the first peak.

Analytical evidence thus indicates that both absorption peaks at  $2833\overset{\circ}{\text{\AA}}$  are by atomic lead and consequently absorption measurements must involve both peaks--or more accurately, the combined areas under both peaks.

It was found that the Pb absorption signals were evolved in a similar pattern. On a given strip chart, the peaks had remarkably reproducible relative half-widths approximating a ratio of 1:3. In cases where the two peaks were not completely resolved, the predominant peak could readily be identified by its half-width. This is of considerable significance because analytical use of peak height must take into consideration differences in half-widths--especially if peak height additions are to be made. A practical method found

for summing peak heights was to treat the areas under the peaks as triangles, and to normalize peak heights with respect to the second peak. Computer programs are being developed to perform this operation.

In recent preliminary experiments in this laboratory, it was discovered that double peaks were eliminated by the substitution of  $\text{HNO}_3$  for  $\text{HCl}$  in sample preparation. A study of the feasibility of using  $\text{HNO}_3$  instead of  $\text{HCl}$  is under way.

A result of the investigations will provide a better overall understanding and subsequent control of the Delves cup AA technique--one of the "prima donnas" of spectrochemical methods, and the information should be applicable to non-flame atomic absorption methods in general.

#### B. Research and Development

##### 2) Emission Spectroscopy

Application of the Hilger prism spectrograph to trace analysis has required upgrading optical performance, principally with regard to stray light. Progress Report PR3, pp. 18-20, described the results of previous work in re-orienting optical elements and addition of light baffles which collectively reduced stray light an order of magnitude over the original performance. Additional work was done to

maximize uniformity of slit illumination to permit one line emulsion calibration and an analytical range of two orders of magnitude from a single spectral line.

A spin off from this work was a simple method for the assessment of parallelism and calibration of slit widths in the 10-50 $\mu$ m range through the application of Fraunhofer diffraction by the slit illuminated by a 5-milliwatt ruby laser. The diffraction pattern projected on a screen placed 1 meter from the slit is sufficiently intense and crisp so that accurate and precise measurement of the width of the first diffraction maximum can be made and correlated to the absolute width at illuminated points along the slit.

A general method has been calibrated for the determination of thirty-four elements on a semi-quantitative basis in materials of plant, animal or mineral origin by direct dc-arc excitation. Required sample size for trace elements is 20 milligrams of the dried sample for the two separate exposures necessary to embrace the wavelength interval representing the elements of interest. Where only major constituents are required, a one-milligram sample is adequate. The method is adaptable to solutions. Working limits of detection range between one nanogram and one microgram of the given element in the electrode. Because of the inverse



relationship of dispersion of the prism spectrograph with wavelength, limits of detection become significantly degraded at wavelengths greater than  $3000\overset{\circ}{\text{\AA}}$ .

A simple device was constructed to conveniently control the number of sector steps exposed in a given spectrogram. The device consists of a slide at the entrance slit similar to the traditional fishtail wedge but having the lower arm of the wedge horizontal so that, on translating the slide across the entrance slit, the aperture height is varied from a fixed point, thereby permitting convenient selection of the number of sector steps in a given spectrogram. Use of the device simplifies routine operation of the spectrograph when variable numbers of steps are required in sequential exposures.

A method has been developed for the direct determination of lead in bone tissue by a vapor-phase selective extraction technique by which lead is preferentially volatilized from the sample matrix during the excitation process. Required sample size is 10mg of ashed tissue. Limit of detection with the Hilger spectrograph is 0.5 ppm on the dried sample basis. Relative standard deviation is  $\pm 15\%$ . Analytical conditions are listed in Table 70.

The vapor-phase selective extraction technique has



TABLE 70

Analytical Conditions for the Determination of Lead in Bone Tissue  
by Optical Emission SpectroscopySample Preparation

50 mg ashed sample  
 50 mg SP-1c graphite powder  
 50 mg SP-2x graphite powder

Standards Preparation

50 mg SP-2x graphite containing lead concentrations in a 1:3 geometric series between 1 and 100 ppm  
 50 mg SP-1c graphite powder  
 50 mg purified bone base\*

\*Yearling femur sections sequentially leached with  $\text{NH}_4\text{OH}$ , EDTA, NaOH and  $\text{H}_2\text{O}$ . Dried and ashed @ 800°C.

Spectrographic System

Spectrograph:	Hilger 1.7 m Littrow
Wavelength Setting:	2240-2900 Angstroms
Auxiliary Optics:	Arc plasma focused on collimator by spherical lens at slit at a magnification factor of 5. Mask at collimator selects central 2mm of arc plasma image.
Slit Optics:	20-um slit width 5-step rotating sector of 1:2 step ratio
Upper Electrode:	U-7 5001 (Ultra Carbon)
Lower Electrode:	U-7 100-L (Ultra Carbon)
Electrode Charge:	40 mg
Excitation Chamber:	ERL Mark I (See PR-3)
Analytical Gap:	4 mm
Excitation:	15 sec. @14 Angstroms (short circuit) dc arc in 20:80 $\text{O}_2$ :Ar gas flow of 14 cfh
Detector:	Eastman 33 emulsion developed 4 min. in D-19 @ 21°C
Photometry:	Pb 2833.07 Angstroms low range Pb 2663.17 Angstroms high range Analytical Curve: $I_{\text{Pb}}$ vs ppm Pb

been applied to the development of a procedure for the determination of baseline levels of cadmium and lead in soil samples. The very low concentrations of cadmium dictated the use of the sensitive but interference burdened Cd  $2288.02\text{\AA}$  line instead of the conventionally used but relatively insensitive Cd  $3610.5\text{\AA}$  line. A consideration of the Hilger spectrographs' dispersion of  $1.9\text{\AA}/\text{mm}$  at  $2288\text{\AA}$  indicated that resolution from the interfering As  $2288.12\text{\AA}$  atomic line could be obtained with a slit width of  $20\text{ }\mu\text{m}$ . Potential problems of spectral interference in the use of Cd  $2288\text{\AA}$  were not by atomic lines, but by molecular systems of  $\text{N}_2$ ,  $\text{O}_2$ , and to a lesser extent, NO under certain conditions of excitation.

An investigation of the variables affecting Cd  $2288\text{\AA}$  line to background intensity and the excitation of molecular systems included electrode geometry, electrode charge temperature, excitation, signal integration times, and composition of ambient atmospheres. Substitution of 80:20 Ar: $\text{O}_2$  for atmospheric air removed the spectral interference by nitrogen molecular systems. The presence of oxygen permitted a flame-like plasma at the relatively low current of 14 amperes dc, and quantitative Cd extraction in 10 seconds. Although these conditions were optimum for cadmium, approximately 20 seconds were required to extract a sufficient

fraction of lead to provide a linear analytical curve over the concentration range of interest. However, at approximately 12 to 15 seconds from the start of excitation, the arc plasma was observed to undergo a transition to the excitation of  $O_2$  molecular systems ( $O+2$  second negative system with persistent band heads at 2285.8 and 2291.8Å which presented spectral interference with the 2288.Å cadmium line).

It was found that a compromised integration period of 14 seconds afforded a calibration for Cd with a limit of detection of 2 ng Cd in the electrode (0.2ppm) and a reasonably linear analytical curve for Pb between 10 and 300 ppm. The relative standard deviation for Pb was between 10 and 15 percent. Analytical calibration was referenced to Cd and Pb concentration values in carefully mixed soil samples previously analyzed by atomic absorption methods.

The overall analytical conditions and electrode geometry are similar to a carrier-distillation system in which a deep-cratered electrode functions as a crucible; and through control of electrode charge geometry and temperature programming, Cd and Pb are preferentially volatilized over a given time interval from the sample matrix into a flame-like plasma with minimal consumption of the electrode.

A sectional view of the sample electrode and atmosphere control assembly is shown in Figure 113.

The resultant spectra, however, were of relatively low integrated intensity not sufficient for developing optimum photographic density in a high contrast emulsion; but by double exposing the emission from two replicate electrode charges, the required photographic density was obtained. By-products of double exposure were signal averaging of duplicate spectra with resultant time savings in densitometry, and also doubling the number of samples per plate. The method has been applied to routine samples of urban soil for the determination of cadmium and lead, and a survey of other heavy metals.

Current experiments are being conducted with pure argon instead of  $O_2:Ar$  mixtures as the ambient gas in the vapor extraction technique for the determination of Pb and Cd in soil and biological tissue. Preliminary results with soil have demonstrated the feasibility of obtaining the required plasma conditions in the absence of oxygen. Though considerably higher arc currents are required to initiate and maintain the flame-like plasma, the absence of  $O_2^+$  molecular interference with Cd 2288 $\overset{\circ}{A}$  permits relaxation of the critical time-temperature control of the Cd integration period.

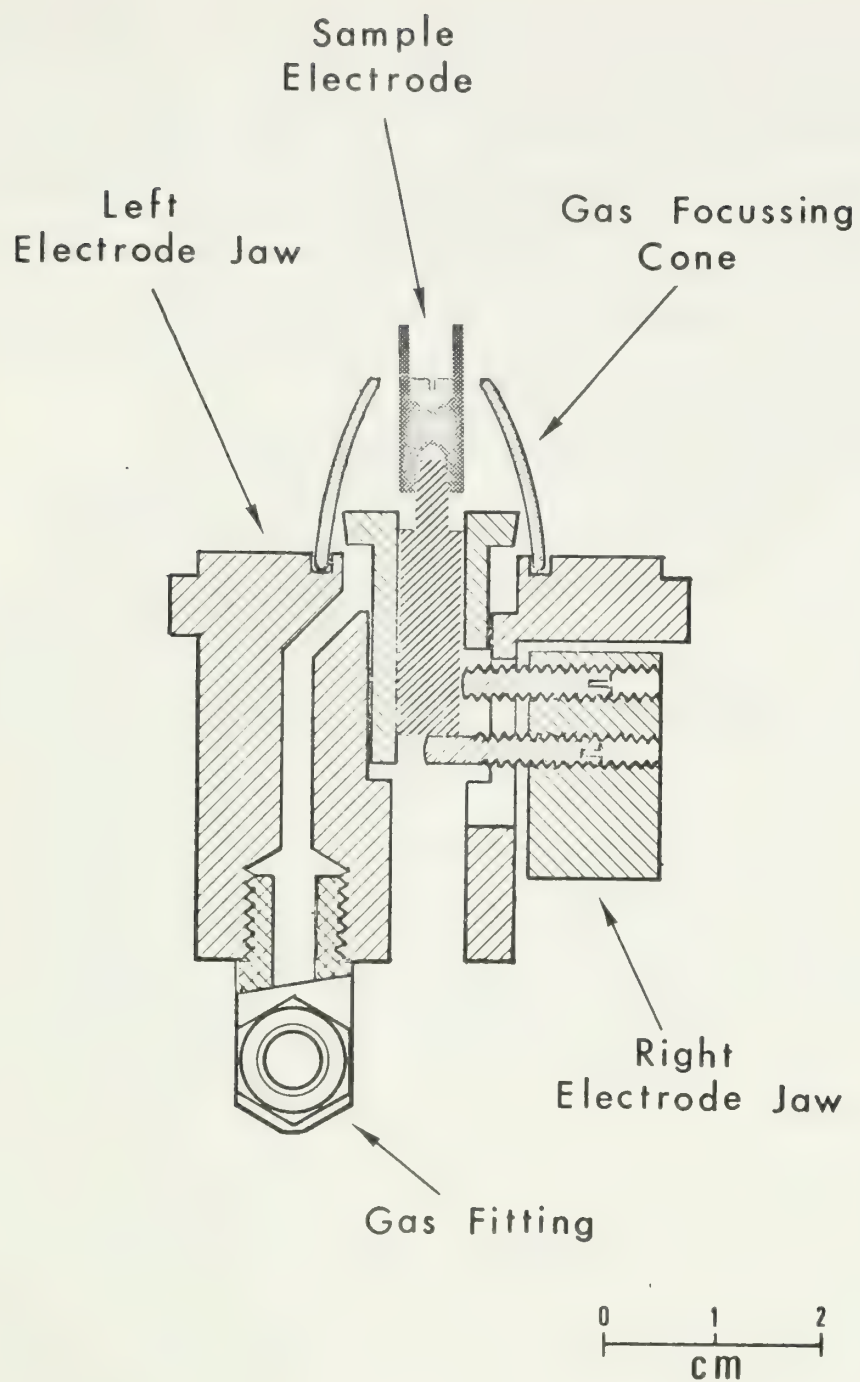


Figure 113 Sample-Electrode Assembly for Excitation  
in Controlled Atmospheres



A potential fringe benefit of the use of Ar instead of  $O_2:Ar$  as the support gas is negligible deterioration of the sample electrode even at arc currents of 30 amperes; and consequently the possibility that sample electrodes may be reused several cycles with significant savings in graphite costs.

#### B. Research and Development

##### 3) Anodic Stripping Voltammetry

During the period covered in PR2 this laboratory had been principally interested in developing a superior carbon-based mercury plated electrode for anodic stripping analysis. Four useful formulations: moderate and high density graphite, pyrolytic graphite and glassy carbon had been found to be superior in a comparative sense to the low density materials then standard equipment for the Environmental Science Associates anodic stripping apparatus. The latter was itself the mainstay equipment for routine ASV work in this laboratory.

Subsequent experience during the ensuing months showed that the inexpensive and readily available high density graphite material manufactured by POCO Graphite, Decatur, Texas (Type-1406R-AQZ-1) to be superior to other types tested on the basis of ease of fabrication, reproducibility, and ultimate electrode surface stability. A slight loss



in sensitivity was noted when compared on an equal gross surface area basis against the most sensitive material, glassy carbon. This difference was difficult to establish because the glassy carbon proved to provide the least stable electrode surface of all materials tried. Further, the material tended to suffer irreversible destruction of the surface properties if subjected to oxygen-evolving anodic potentials for any length of time.

These electrodes and a prototype single cell apparatus using a Sargent Synchronous Rotator and a Heath Operational Amplifier Polarograph replaced the ESA equipment as the routine ASV unit in March, 1973. At the time of transition the overall precision of ASV assays with ESA equipment was limited by a poor (28%) repeatability and severe variability in electrode sensitivity sufficient to require standard addition calibration for every sample. In contrast the single POCO graphite electrode had an initial repeatability of less than 8% and was sufficiently stable as to require standard additions to be performed only every 5-10 samples.

The simple ringstand and clamp single cell apparatus has evolved over the past several months to the multi-cell unit shown in Figure 114. The repeatability achievable with



Figure 114

Multi-sample Anodic Stripping Unit

this unit is shown by the repeated tracings of Figure 115 which were obtained with a sample of human tooth. Due to the large amounts of calcium and phosphate, undestroyed residual organic matter, and high acidities necessitated by the method of dissolution these samples are often characterized by poor reproducibilities. The protected and reproducible environment afforded by the cell chamber together with increased attention to timing and sequencing of procedural steps has improved the precision to repeatability to the typical figure of Figure 115 of 1.24% relative standard deviation. The net result is that instrument and measurement precision components are not significant with respect to other variables such as prior treatments or sample storage. Electrode stability is sufficiently good that standard additions now serve primarily as a check on the surface condition of the electrode and evidence of a need to replat rather than an actively used measurement variable.

The unit shown in Figure 114 has evolved as the result of prototype testing using the ringstand-clamp cell unit. Each component was evaluated on the basis of: peak shape, sensitivity, and reproducibility. Accuracy was not used as a criterion for two reasons: an earlier in-house study had shown no significant differences between results obtained by the

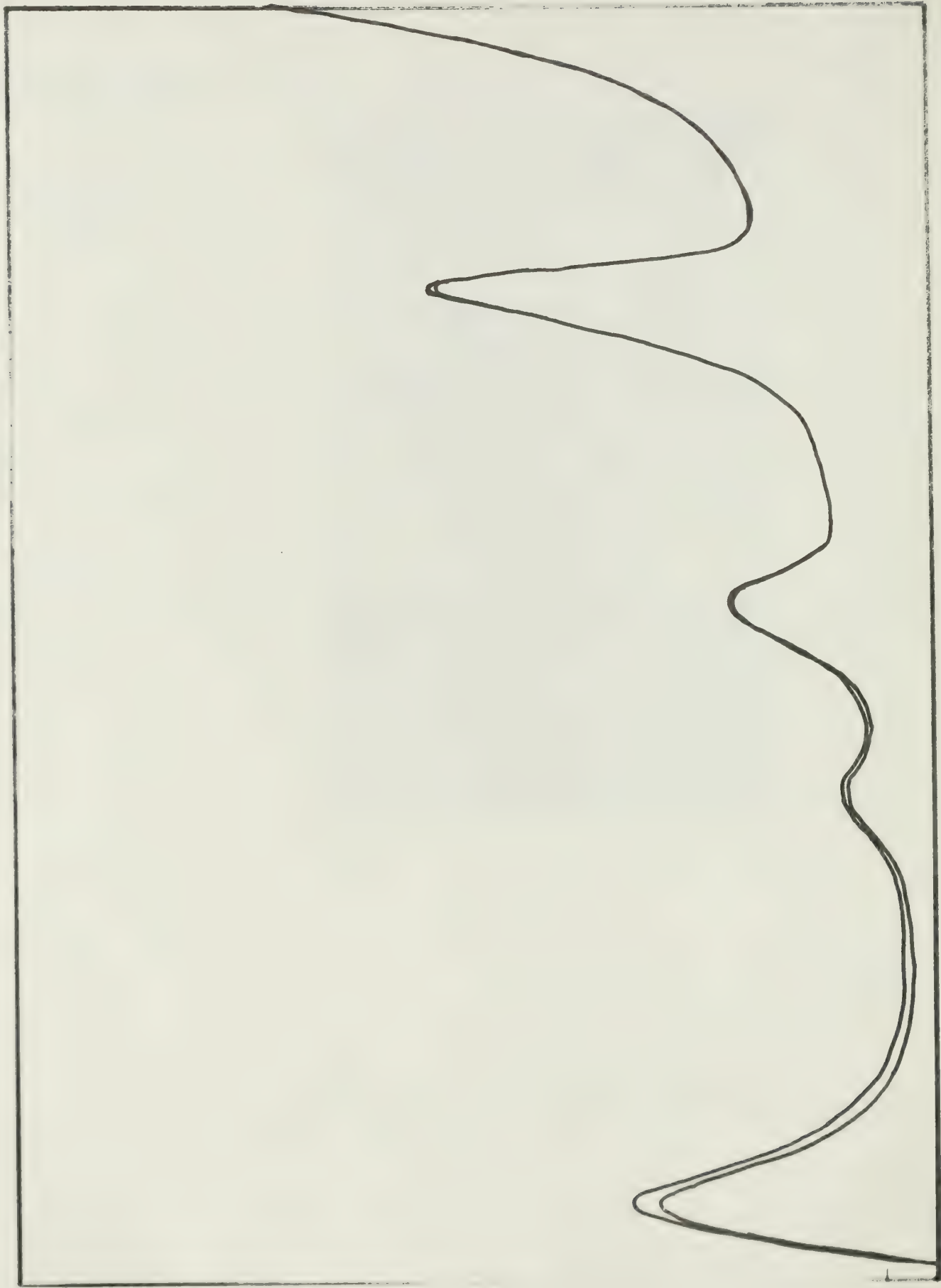
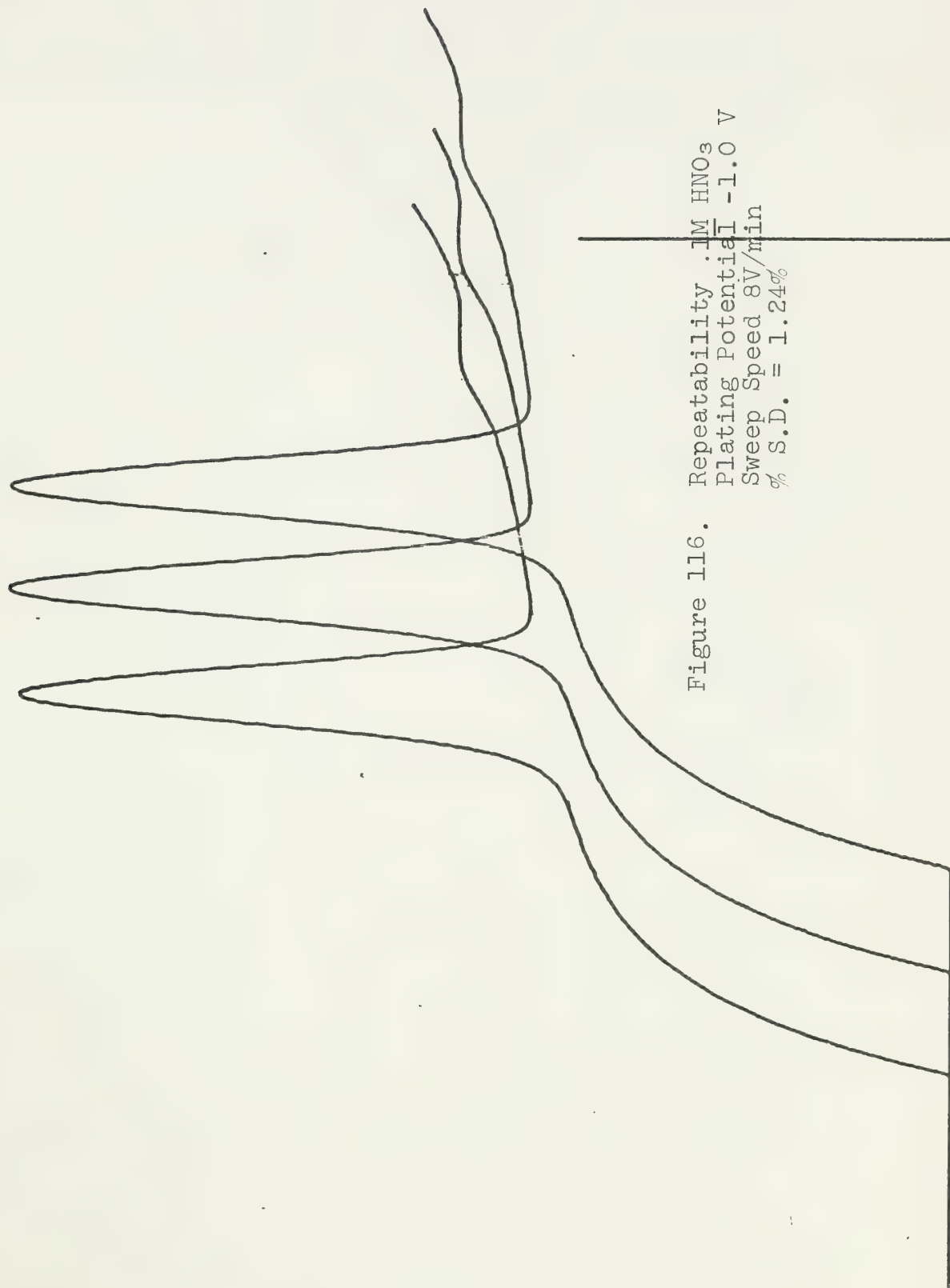


Figure 115. Repeat Tracing of Tooth Solution. 4 min plate sweep speed 8V/min in .08M HNO<sub>3</sub>. Plating Potential -1.2V.



prototype single cell and by atomic absorption and the only AA method capable of measurements at concentrations comparable to those common to ASV was much more impressive (8-15%) and in constant routine use.

The unit consists of a 6 inch (diameter) x 10 inch section of Plexiglass closed at both ends to provide a partially air tight housing for a Lazy Susan wheel bored to hold 12 30x90mm Pyrex sample cells. Indexing slots on the wheel engage partial guide rails to permit sample cell changing by lowering the wheel and rotating it to the next position. The active area of the graphite electrode requires a minimum sample volume of 7 ml; in practice a standard 10ml volume has been adopted. Intersample contamination by residual holdup on the electrodes and compartments has been found to be negligible for water samples because the sample-to-sample variation in metals content is usually small. Since this will not be true for the general sample with large variations in content the glass compartments are now being replaced by non-wetting plastic equivalents.

The system provides for constant nitrogen sparge for 10 of the 12 cell positions simultaneously. The remaining two positions immediately in front of the door have no gas inlet tube to allow easy sample cell loading. Oxygen acts



destructively in this form of ASV primarily by destroying the mercury plate. This is manifested in decreased sensitivity, peak broadening, appearance of extraneous satellite peaks, and a drifting residual current base line. Electrode sensitivity is sufficient to obtain accurately measurable peak currents with 2 minutes stirred electrolysis - a time that is too short for complete sparging for the first sample to be assayed. This is eliminated as a variable by sparging for 10-15 minutes before the first sample is run. After this length of time further sparging does not apparently create any further improvement in performance - the sparge is continued for all samples simply to maintain this condition. A deoxygenating and humidifying wash tower train is inserted in the nitrogen tank gas line to prevent excessive sample evaporation.

Anode (Pt) and Reference (Ag/AgCl) electrodes are isolated in 5mm pyrex tubes terminating in porous Vycor plugs attached by heat shrinkable Teflon. These and the electrode leads are brought out through the unit wall through adjustable screw attached blocks to stabilize interelectrode distances. Electrical connections are made through mini-Amphenol connectors and shielded cable. A three pole-double throw center off switch on the electrolysis unit permits

controlled synchronization of electrode motor, chart recorder pen with the three phases of measurements: collection electrolysis, potential sweep, and anodic potential electrode cleansing. Studies are presently in progress to determine the best means of replacing this switch with an accurate timer mechanism which should improve precision and ease of operation.

Successful fabrication of the single cell prototype has permitted a number of electrochemical investigations which were not possible with the older ESA apparatus. Heretofore, such studies were limited to those with effects large enough to be discerned under the cover of a large overall imprecision of measurement. For example, a previous attempt to quantify the effect of nitrogen flow rate in the ESA-Matson apparatus where sparging is the sole form of mass transport met with no success because the effect could be seen only for the trivial condition of no flow at all. Further, it has proved possible to maintain electrode and solution integrity for periods of at least 12 hours thus permitting long time scale investigations requiring repeated examination of the same solution. An additional advantage has been a much shortened and improved learning period for new technicians. The average three minutes per sample operation time results in approximately ten times the number

of practice experiments that can be performed in any given period. With the single exception of accidental loss of mercury plate by anodization there are no reasonable missteps in procedure that cannot be recovered by rerunning the same solution correctly since no substantial changes in solution composition take place as a result of measurement.

As a result of the Trace Metals Symposia held for the past two years at this University and other statewide publicity about the Institute for Environmental Studies this laboratory attracted the volunteer half-time services of Mr. Raymond Robbins during the summer session of the university. Mr. Robbins gave of his time in return for the experience of active participation in an environmentally oriented laboratory. He elected to work on a small research problem concerned with developing optimal conditions for the ASV determination of Bi. The laboratory at present does not have an active demand for such a capability so the pressures of becoming skilled quickly were removed. An initial investigation into the ASV determination of antimony proved negative. No stripping peak could be obtained in solutions of common anions:  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in either neutral or acidic pH. Since it is known that this element can be deter-

mined in a tartrate medium the project was abandoned. Bismuth shows a very well behaved stripping voltammetry in dilute (0.01M)  $\text{HNO}_3$  with a peak potential of -0.15 vs Ag/AgCl. For plating times from 0.5 to 5 minutes the resultant peak height was approximately proportional to plating time tending to fall below the extrapolated straight line for longer times. This behavior is not explicit in anodic stripping theory and has been approximated several times before in this laboratory for Pb, Cd, Cu and Tl.

The large area electrodes and manner of solution mass transport used in ASV studies preclude any accurate assessment of the nature of the anodic process on ab initio theoretical grounds. It was of interest to establish with some certainty that the process for Bi was the most expected 3 electron oxidation to  $\text{Bi}^{+3}$ . At the time this work was done it was the collective conventional wisdom of practitioners of ASV that every element had its own peak current - concentration value. This has subsequently been shown (vide infra) not to be the case. In the absence of complicating inter-metallic interactions and nonoverlapping peak heights for equal molar concentrations of metals should stand as the ratio of the number of electrons involved in the rate limiting step. Initial results compared between Pb and Bi showed the latter peak height to be approximately 50% greater than

for an equal concentration of Pb. However, the nitrogen sparge stirring mode used in these experiments is sufficiently variable if the gas flow rate has been altered that it was necessary to carry out a prolonged sequence measurement under constant conditions using a direct comparison. A test solution of 10 ppb Bi was electrolyzed for varying lengths of time recording peak heights under constant stripping conditions. Results are shown in the top half of Table 71. A repeat of the initial short time condition was performed again at the end of the set to establish that the electrode did not accumulate Bi. Following this set a micro-volume addition of 10 ppb Pb was created and a repeated set of electrolyses shown in the bottom half of Table 71 was done. Results of peak height comparison for the two elements electrolyzed together against the same solution when it contained only Pb shows an apparent exaltation of Pb by Bi for the shorter plating times but no effect at the longer times of 5 minutes. The effect - although slight (ca. 10%) - is not negligible if real. The coincidence of the electrolysis time at which the effect seems negligible and the time when the  $i_p$ -t curve begins to flatten out seriously may reflect simply a failure to observe the effect due to a diminished measurement sensitivity at



Table 71

## ASV Analysis of Bismuth Lead Test Mixtures

<u>Run</u>	<u>Comment</u>	<u>Pb <math>\mu</math>a reading</u>	<u>Time</u>	<u>Bi <math>\mu</math>a reading</u>
0	Blank	1	5 min.	-
1	Add 5 ppb	3	0.5	-
2	Lead	5	1	-
3		7	2	-
4		9	3	-
5		11	4	-
6		11.5	5	-
7		5	1	-
8	Add 5 ppb	3	0.5	6
9	Bismuth	4.5	1	8
10		6	2	10
11		8	3	13
12		10	4	15
13		11.5	5	16.5
14	Add 5 ppb	6	0.5	12
15	Pb and	8	1	15
16	Bi	12	2	21
17	(both	15.5	3	25
18	at 10 ppb)	19	4	30
19		22	5	33
20		8	1	13.5



at that point. Unfortunately lack of time precluded running the reversed experiment of adding Pb to a Bi solution. The latter would have permitted an answer to the question of whether the effect is mutual as it should be if there is an intermetallic interaction. A repeat of this study using the improved rotating electrode would be of value particularly if coupled with the kind of study typified by the work reported in the following section.

#### Effect of Plating Potential on ASV Sensitivities

Theoretical equations for stripping voltammetry predict that for the thin layer "diffusion free" case the peak height for an element soluble in mercury with no interactions should compare with another under the same conditons differing only by the ratio of electrons involved in the process. Examination of the literature reporting working analytical methods in the vast majority of cases does not include the kind of data to substantiate whether this condition holds for the electrodes not amenable to theoretical treatment. For the two reports which do contain the necessary observations the contrary seems to hold: each element has a unique peak current concentration relationship. This situation makes it very difficult to make valid comparisons

between methods or laboratories or equipment. The ad hoc unexpected estimation of an unexpected element in a sample may fail unless the operator has access to standard solutions of every element of interest. Experiments performed in this laboratory of which Figure 117 is typical show that the expected theoretical behavior can be obtained but apparently not under conditions commonly used. As the initial plating potential is made increasingly negative the ratio of Cd to Pb peak heights approaches a constant which is unity for equal concentrations. This is a necessary but not sufficient condition; of equal importance is the supporting electrolyte. In the case of Cd-Pb a chloride medium is required. The amount of overpotential to achieve this condition is surprising: a minimum of 600mv for Cd and 850 for Pb using anodic peak potentials as references. Cyclic voltammograms of the two elements using similar electrodes similar to those presently in use showed a measurable degree of irreversibility for Cd and Pb on the order of 60-70mv, but not enough to account for the large driving potentials apparently necessary. It is possible that the copious bubbles of hydrogen evolved at these negative values tend to act as an efficient electrode cleaner and/or promotes stirring in the micro-vicinity of the surface. The former is well known in other electrochemical fields but the latter

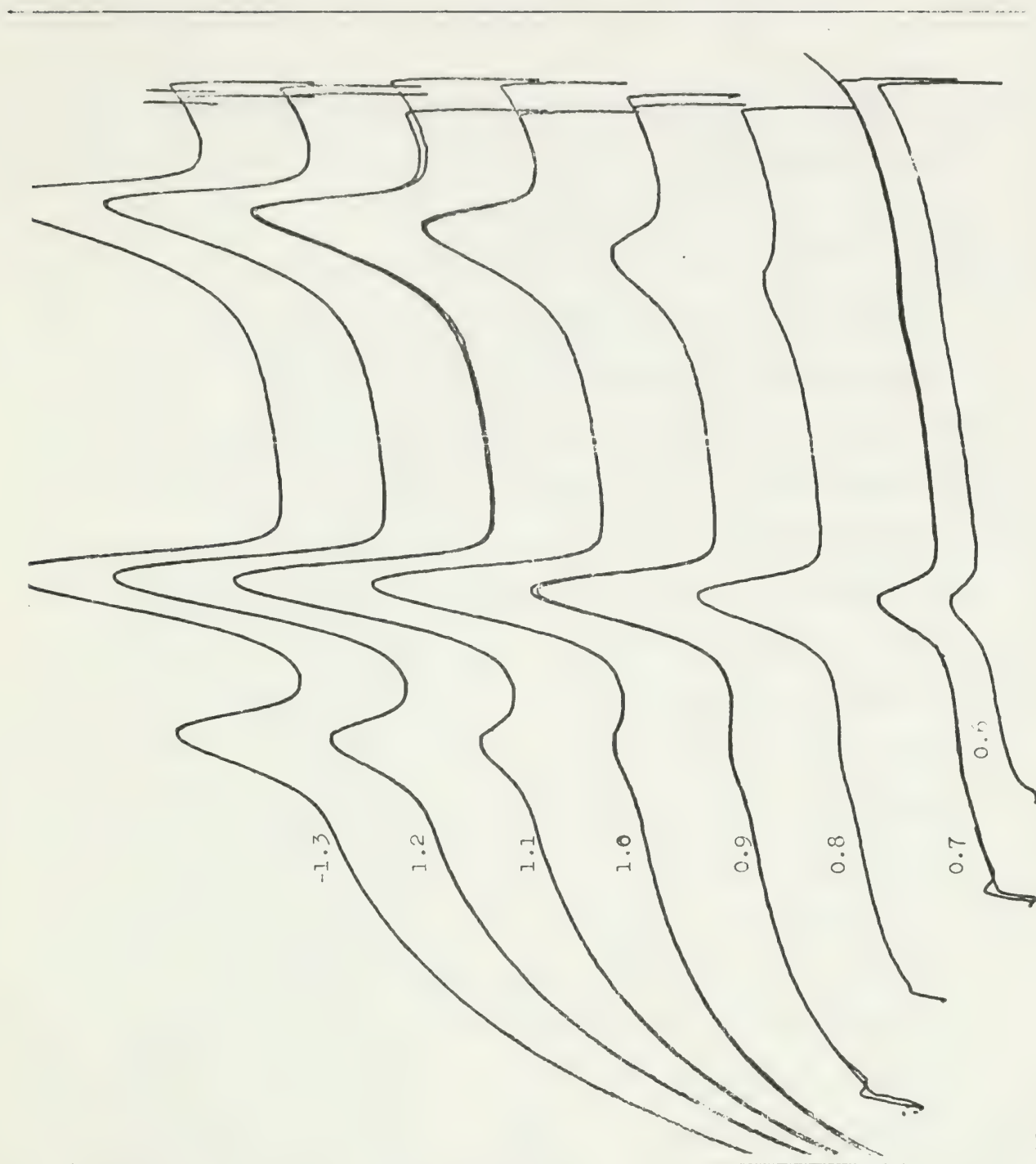


Figure 117. Effect of Plating Potential on ASV. Determination of Cd, Pb and Cu.

is in direct contradiction to studies made of the hydrogen evolution reaction.

#### Anodic Stripping Behavior of Mercury

The sensitivity of anodic stripping assays increases as the thickness of the mercury film decreases. Sensitivity also increases as the voltage sweep speed increases but this also diminishes the thickness of a film which is "thin" in the sense of optimum response. For most of the ASV work reported from this laboratory the mercury films used have been made deliberately thick. The sacrifice in sensitivity for routine assays is more than compensated by the longer lifetime of the mercury plate.

The present plating procedure involves the mechanical act of wiping the old film residue from the electrode. It was of interest to examine alternate, operator-free means of replating or renewing the electrode surface as part of a long range program to fabricate a completely automated field-installable ASV unit. Initial experiments indicated that it might be possible to remove the mercury film reliably by a controlled cycle of anodic polarizations to remove the mercury electrochemically then to replate in analogous fashion. Our past experience had shown that it is also possible to irreversibly damage the graphite substrate

surface by extreme anodic excursions. A major question was then: can the mercury film be removed with potential excursions which do not destroy the substrate?

Earlier work by Cox and Hiebert (Ph.D. Theses, UI, 1968) had shown that it is possible and convenient to produce mercury films of controllable thickness on platinum by the technique of chronopotentiometry. In this constant current mode the mercury of unknown thickness is oxidatively removed until the monitored electrode potential indicates total loss of the film as shown by a potential shift further in the oxidizing direction. At this point the direction of current flow is reversed with the potential again monitored. The process is repeated cyclically until the electrolysis times for the removal and replating are equal indicating a process occurring with 100% current efficiency. One final cathodic (plating) event carried out at constant current for a predetermined time produces a film of controllable and known thickness through applications of Ohms Law, Farraday's Law, and electrode geometrical expressions.

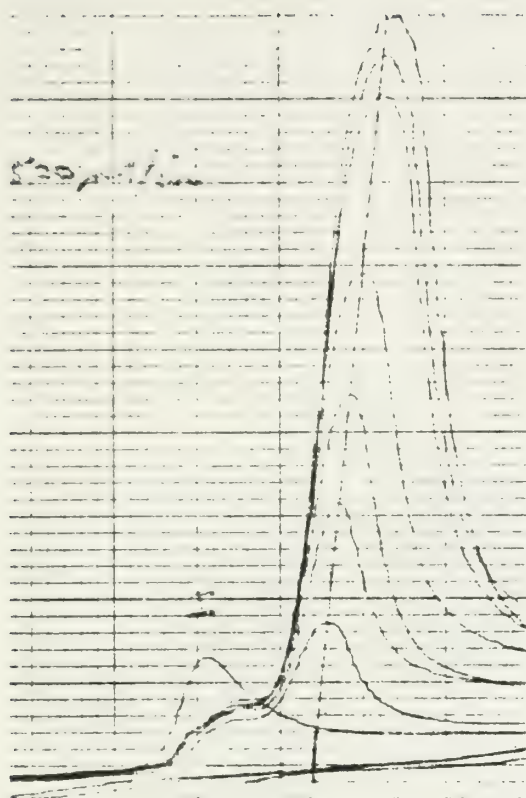
Analogous experiments using linear potential sweep modes are not as straightforward in that it is the potential not the current which is controlled hence quantitative calculations require area integration of potential-time curves. An advantage is that direct potential control is a better control



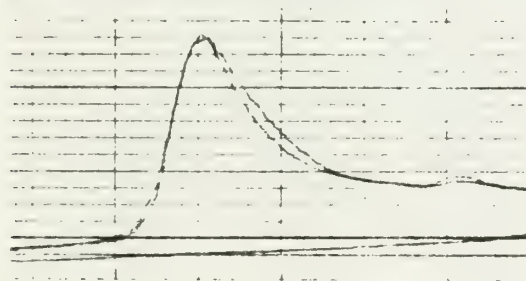
over the nature of any electrochemical process that might occur at the electrode surface.

The results shown in Figure 118 are a composite of several experiments using different sweep modes, solution conditions and electrode treatments. Of primary interest is the comparative behavior of the electrode in chloride and nitrate and the anodic-cathodic behavior on recycling. In the presence of  $\text{Cl}^-$  the processes are dominated by the pronounced and early process of the anodic formation of an insoluble film of  $\text{Hg}_2\text{Cl}_2$  on the electrode surface in a not very reproducible manner. (Figure 119) This is followed by (Curve 1) by additional processes we have tentatively identified as: oxidation of Hg to  $\text{HgCl}_2$  and oxidation of ultimate surface Hg at the more positive potential. The corresponding curve for nitrate medium is simplified by the elimination of the calomel formation reaction and is believed to consist only of direct oxidation of film Hg to  $\text{Hg}^{+2}$  followed by the removal of the ultimate film. In neither case is it possible to completely recover the oxidized products by cathodic cycling. Residual interest remains in the observation that cycled electrodes seem to replate extremely easily provided the ultimate film has not been removed. Further research may show that a partial electrochemical stripping by controlled potential at a value insufficient to remove the final film

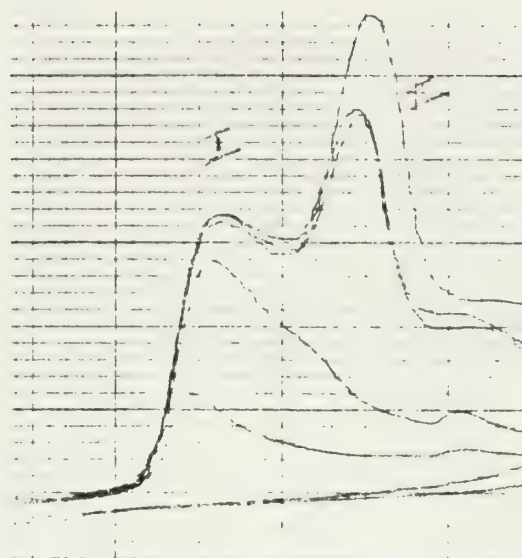




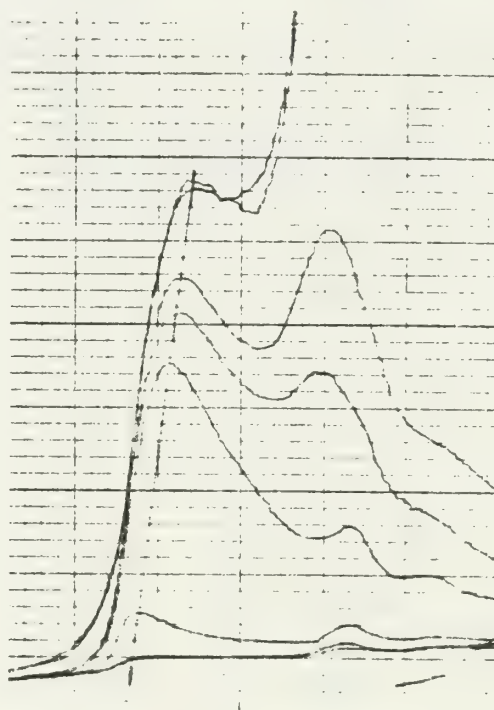
A. New Plating Solution



B. After Electrode Has Set  
90 Minutes

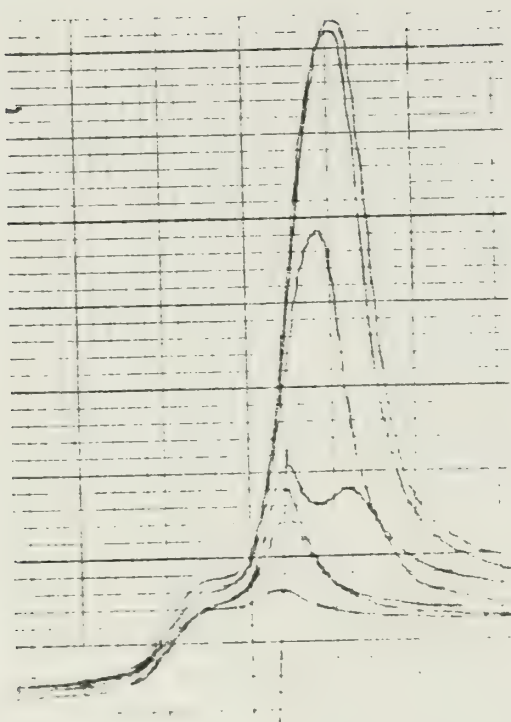


C. Repeated Platings

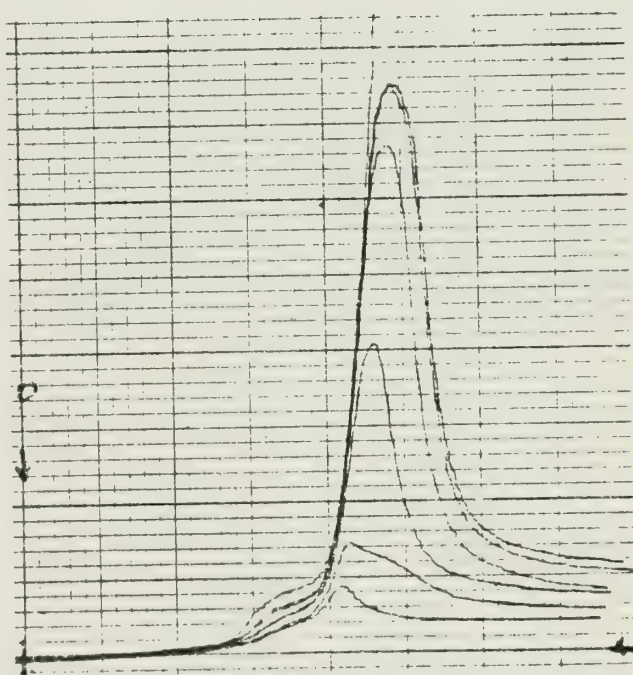


D. Repeated Platings  
After 300 Minutes

Figure 118. Effects of Solution Conditions



E. Wiped Test Electrode  
Clean, Plate With  
Fresh Plating Solution



F. New Plating Solution Made  
From  $\text{HgNO}_3$  in  $0.05\text{M}$   $\text{HNO}_3$

Figure 118. Continued

Mercury Buildup on GC-10

$t_{el}$  - 2min.

$E_p$  - -100mv vs Ag/AgCl

Sweep - 2v/min.

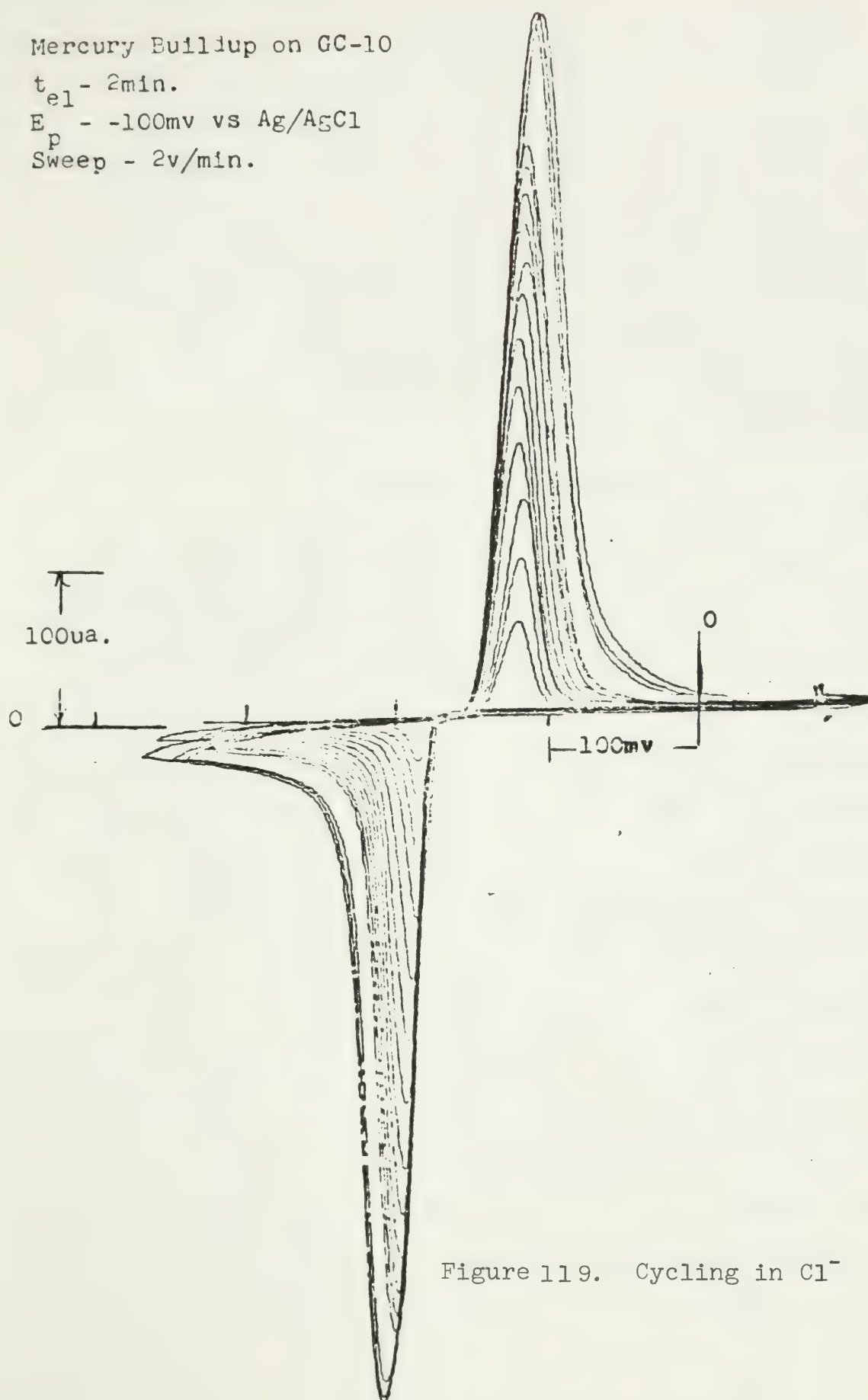


Figure 119. Cycling in  $Cl^-$

may produce a satisfactory sub-film base for subsequent constant current controlled plating of a moderately thin film layer of mercury. At the present time it does not appear possible to produce a replated electrode which can be reliably reconditioned solely by potential-time-solution medium controls.

#### Anodic Stripping Behavior of Copper

Experience in this laboratory with a wide variety of ASV samples has shown copper to be practically ubiquitous in the final solutions. A non-negligible and detectable amount (1-10ppb) appears as the result of prior chemical treatments using reagents not specifically cleansed of the element. A number of observations have been made that suggest copper to act destructively with respect to the anodic stripping determinations of other elements, e.g., Bi, As, Sb, Cd, Tl, and possibly Pb. A small project involving the determination of Pb in children's teeth being carried out in these laboratories has expressed an interest in the additional determination of copper. A program of determining the optimum ASV conditions was begun with the final objective of creating a satisfactory determination procedure for copper. Secondary objectives were to determine the extent of copper interference with other elements

and to establish a means of correcting or eliminating the interference.

Figure 120 typifies the ASV behavior of copper in nitrate and chloride supporting acidic electrolytes. The element is quite sensitive to the presence of Cl as supporting electrolyte as shown by the repeated curves in Figure

following the successive additions of HCl. The last curve has reached the condition where copper has less than 1/5th the sensitivity of Pb in the same solution. Curve 1 of the following figure resulted from the same solution as was used for the last curve of the previous set after several fuming evaporations with  $\text{HNO}_3$  to remove Cl. The sensitivity returns to a more reasonable figure. In both cases the curves exhibit more satellite peaks than can be satisfactorily explained at present.

One unexpected and unexplained result was the observation that copper could be determined with the same sensitivity as for Pb in the same solution by resorting to the extremely negative plating potential of -1.5 volts vs Ag/AgCl in a nitrate electrolyte. This limits the flexibility of ASV assay when copper is sought because the necessity for nitrate as an ion is contrary to the requirement for Cl medium for successful determination of Cd. The extreme differences between necessary cathodic collection potential and the



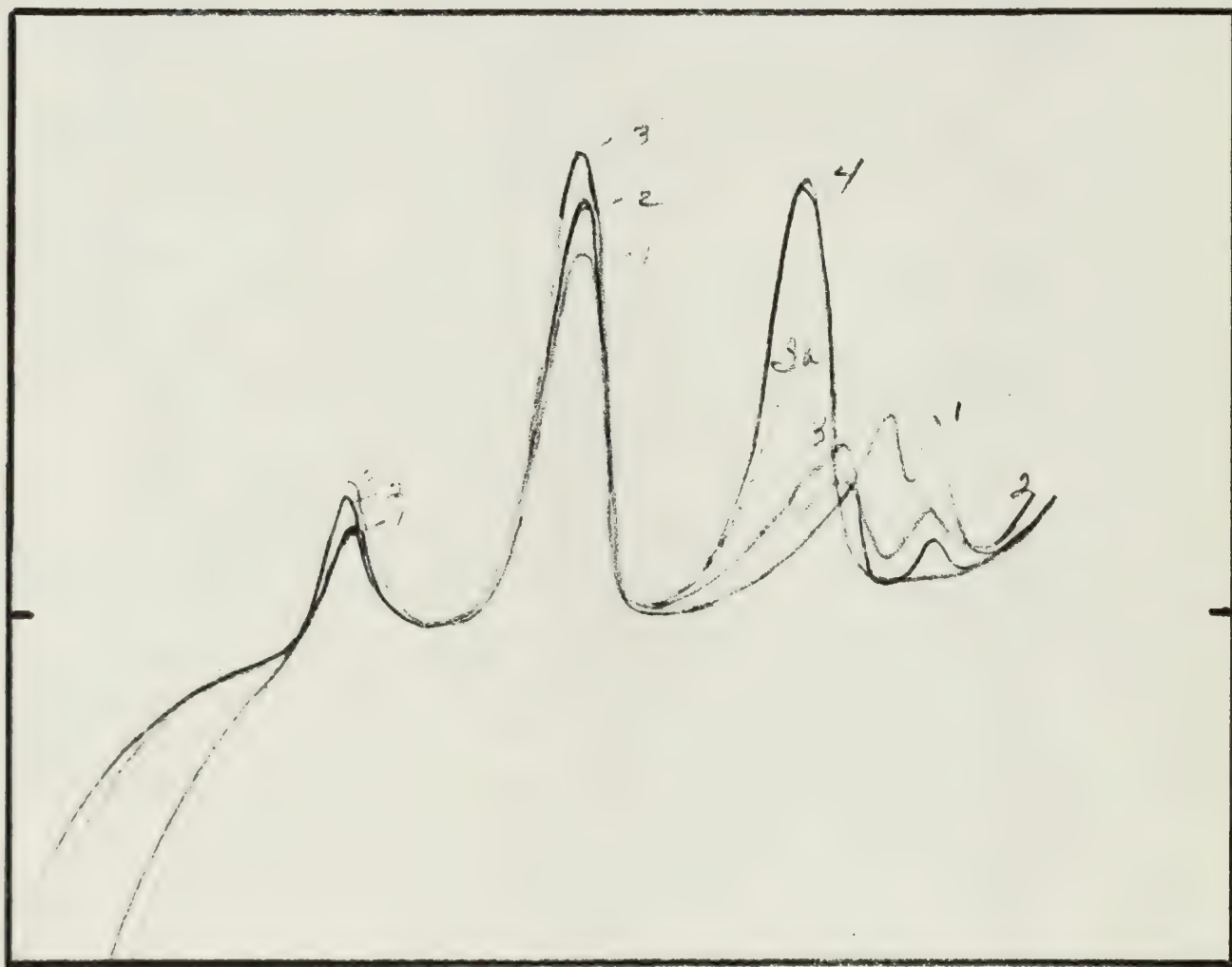


Figure 120. Effect of HCl on ASV Curves for Pb, Cd and Cu: (1) 0.012M, (2) 0.024M and (3) 0.060M HCl (microvolumetric additions). Curve 3a is solution 3 with 2ppb additional Cu added. Curve 4-solution 3a in 0.05M  $\text{HNO}_3$  after fuming to remove  $\text{Cl}^-$ .



stripping peak potential and the presence of satellite peaks strongly suggest the intervention of intermetallic compound formation between copper and the mercury film or additional metals in the amalgam. Past work by Cox and Hiebert showed that such interactions in the case of platinum substrate electrodes could be moderated by the addition of Ag in doping level amounts to the mercury film. It has been reported that alternative doping with gallium is effective for copper. Research is now underway to investigate these alternatives.

## References

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- 2) F. Fernandez & H. L. Kahn, *Atomic Absorption Newsletter* 10, 1 (1971)
- 3) A. A. Cernik, *Atomic Absorption Newsletter* 12, 6 (1973)
- 4) R. W. Pearse & A. G. Gaydon, "Identification of Molecular Spectra," Wiley, New York

# V I I I.            A P P E N D I X

## A. Personnel

### 1. Administration

#### Coordinating Committee

- B. B. Ewing, Professor of Sanitary Engineering;  
Director, Institute for Environmental Studies
- H. A. Laitinen, Professor of Chemistry;  
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- W. R. Boggess, Professor of Forestry; Head of  
Department
- J. B. Hanson, Professor of Plant Physiology;  
Head of Department of Botany
- R. L. Metcalf, Professor of Zoology and Entomology
- J. T. Pfeffer, Professor of Sanitary Engineering;  
Member, Advisory Panel on Pollution Abatement  
Policies
- G. W. Salisbury, Professor of Dairy Science;  
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#### Steering Committee

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- G. L. Rolfe, Co-Principal Investigator, Total  
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- B. B. Ewing, Director, Institute for Environmental  
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- A. M. Hartley, Director, Analytical Chemistry  
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- J. L. Hudson, Modeling Team
- D. E. Koeppe, Soil-Water-Air-Plant Continuum Group
- G. Provenzano, Social Studies
- W. von Fischer, Assistant Project Director

Administration

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A. D. Baxley, Clerk-Typist  
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 K. I. Moller  
 K. Schemske  
 R. E. Veltman

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 D. E. Koeppe, Assistant Professor of Plant  
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 H. V. Leland, Assistant Professor of Environ-  
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 R. J. Miller, Professor of Soil Physical  
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 F. J. Stevenson, Professor of Soil Chemistry

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J. E. Bittell  
R. R. Gadde  
C. P. Malone  
S. S. Shukla

## Research Assistants

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F. J. Drone  
J. Wedding  
C. Downing

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R. A. Root

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Biochemistry

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D.F.S. Natusch, Assistant Professor of  
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J. Simon, Professor Veterinary Pathology  
A. R. Twardock, Professor of Veterinary  
Physiology



Research Associate

K. P. Li

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J. L. Shonkwiler

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T. W. Daggett

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G. L. Wheeler, Associate Research Biologist

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R. M. Forbes, Representing Animal Processes

A. W. Haney, Representing Plant Ecology

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Assistant Research Engineer

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P. R. Homan

D. A. Luery

F. Markus

M. R. Zaryouni

Student Help  
S. J. Miller

B. SPECIAL PROJECT SEMINARS

November 9, 1972	Disposal of Liquid Digested Sludge on Crop Land Dr. Robert L. Jones, Associate Professor of Soil Mineralogy and Ecology, Department of Agronomy, University of Illinois
November 14, 1972	Properties of Hydrous Oxides Dr. Alan Posner (Australia)
February 23, 1973	Power Particles and Pulmonary Poisons - The Toxicity of Submicron Particles in Air D. F. S. Natusch
May 8, 1973	Control of Particulate Lead Emissions from Automobiles Dr. Emmett Jacobs of E. I. du Pont de Nemours & Co., Inc.
May 23, 1973	Biotron Facility for Controlled Environmental Research, located at the University of Wisconsin Dr. Ladd C. Prosser, Professor of Physiology and Zoology
May 25, 1973	Analysis of Petroleum for Trace Metals R. Hofstadter, Exxon Research and Engineering Co.
May 29, 1973	Lead in the Environment H. A. Laitinen, at Texas A & M University
September 28, 1973	The Transport of Ionic Metal Species Through Membranes D.F.S. Natusch, Analytical Chemistry Division, University of Illinois

## C. METALS PROJECT PROGRAM REVIEW

November 20, 1972

### Opening Remarks

H. A. Laitinen, Director, Metals Task Force,  
Environmental Studies Program

### Analytical Laboratory

A. M. Hartley, Director

### Analytical Laboratory Reports

A. M. Hartley, R. S. Vogel, N. Watkins

### Soil-Water-Air-Plant Continuum Team Reports

H. A. Laitinen, Team Leader

### Chemistry Particulates

K. W. Boyer

### Lead-Hydrous Oxide-Clay Interactions

H. A. Laitinen & R. R. Gadde

### Plant Uptake Studies

R. J. Miller & D. E. Koeppe

### Plant Processes Team Reports

F. A. Bazzaz, Team Leader

### Membrane Binding with Lead and Cadmium Effects of Cobalt and Zinc on Isolated Corn Mitochondria

R. J. Miller & D. E. Koeppe

### Mechanisms of Photosynthesis

Dr. Govindjee & Maarib Bakri

### Effects of Lead and Cadmium on Gas Exchange Properties of Whole Plants and Detached Leaves

F. A. Bazzaz

### The Aerosol Generator

J. J. Stukel & J. Wedding

Luncheon Talk, Dr. Robert Rabin - Environmental Aspects  
of Trace Contaminants - Supported by NSF-RANN

Animal Processes Team Reports

R. M. Forbes, Team Leader

Aspects of Lead Accumulation and  
Metabolism in Animal Tissues  
R. M. Forbes

Interactions of Heavy Metals with  
Phospholipid Membranes  
D. F. S. Natusch

Interactions of Lead with Red Blood Cell  
Membranes  
G. L. Jendrasiak & Linda Bonen

Total Ecosystem Team Reports

G. L. Rolfe, Team Leader

Traffic Monitoring  
R. H. Wortman & V. C. Weaver

Soils and Plants  
A. W. Haney

Small Mammals  
L. L. Getz

Insects  
P. W. Price

Aquatic Systems  
R. W. Larimore & J. McNurney

Aufwuchs  
H. V. Leland & J. A. Baker

Water Sampling  
G. L. Rolfe

Modeling Team Reports

B. B. Ewing, Team Coordinator  
G. L. Rolfe, Team Leader

Introduction  
B. B. Ewing

Atmospheric Modeling  
J. J. Stukel & J. L. Hudson

Ecosystem Modeling  
J. W. Melin & A. A. Chaker

Soil, Plant Modeling  
G. L. Rolfe

Animal Modeling  
J. Abdelnour

Economics  
G. Provenzano

Evening Lecture - Dr. George W. Wetherill, Professor of Geophysics and Geology, Department of Planetary and Space Science, University of California, Los Angeles: "Use of Stable Isotopes of Lead as Tracers in Environmental Problems"

#### D. THIRD TRACE METALS SYMPOSIUM

November 21, 1972

Discussion Session I - HEAVY METALS AND ANALYTICAL METHODOLOGY  
Rapporteur: Dr. S. R. Koirttyohann, Department of Agricultural Chemistry, University of Missouri

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Manuel Brandt, Ethyl Corporation, Ferndale, Michigan  
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J. W. Mitchell, Bell Laboratories, Murray Hill,  
New Jersey  
Cullie J. Sparks, Metals and Ceramics Division,  
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Tennessee  
Ian M. Stewart, Walter C. McCrone Associates,  
Chicago, Illinois

Discussion Session II - HEAVY METALS AND ATMOSPHERICS  
Rapporteur: Dr. H. W. Edwards, Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado



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- M. T. Mills, Oak Ridge National Laboratory, Oak  
Ridge, Tennessee
- E. P. Parry, North American Rockwell Science Center,  
Thousand Oaks, California
- R. J. Thompson, U.S. Environmental Protection Agency,  
Research Triangle Park, North Carolina
- G. S. Wilson, Department of Chemistry, University of  
Arizona, Tucson, Arizona

Discussion Session III - HEAVY METALS AND WATER, SEDIMENTS  
AND SOILS

Rapporteur: Dr. K. J. Yost, Department of Pharmacology  
and Toxicology, School of Pharmacy and Pharmacal  
Sciences, Purdue University, Lafayette, Indiana

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- G. Milburn, U.S. Environmental Protection Agency,  
Enforcement Division, Chicago, Illinois
- C. Stephens, U. S. Environmental Protection Agency,  
Cincinnati, Ohio
- R. E. Wing, North Regional Research Laboratory,  
Agricultural Research Service, USDA, Peoria,  
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## Discussion Session IV - HEAVY METALS AND BIOLOGICAL SYSTEMS

Rapporteur: Dr. R. I. Van Hook, Ecological Sciences Division  
Oak Ridge National Laboratory, Oak Ridge, Tennessee

## Contributors:

- G. C. Battistone, Department of the Army, United States  
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P. D. LaFleur, Activation Analysis Section, Analytical  
Chemistry Division, National Bureau of Standards,  
Washington, D. C.  
Gary Ter Haar, Ethyl Corporation, Ferndale, Michigan

#### E. PROJECT - RELATED LECTURES, MEETINGS, AND PUBLICATIONS

##### Lectures

October 31, 1972 and November 1, 1972	Overview of Effects of Trace Metals H. A. Laitinen; Biological Uptake and Distribution of Lead in Animals by Jamal Abdel nour At Environmental Resources Conference Cycling and Control of Metals held at Battelle Memorial Institute in Columbus, Ohio
November 2, 1972	Trace Metal Interactions and Mobility in Soils O. C. Braids at Eastern Analytical Symposium on "Forms and Species of Heavy Metals in the Environment"
December 29, 1972	Impact of Leaded Gasoline on Man's Environment H. A. Laitinen at AAAS section on Chemistry (C) and Physics (B) in Washington, D. C.
January 8, 1973	University of Illinois Metals Task Force Gary L. Rolfe
January 9, 1973	Organization of an Interdisciplinary Research Project on Environmental Effects of a Pollutant and; The Role of Analytical Chemistry in Interdisciplinary Environmental Science at Twenty-Sixth Annual Symposium on the Analytical Problems of Air Pollu- tion Control at the Louisian State University in Baton Rouge H. A. Laitinen

- January 22, 1973      Introductory Remarks at the Case  
Western Reserve University Frontiers  
In Chemistry Symposium-Environmental  
Analytical Chemistry  
H. A. Laitinen, at Cleveland, Ohio
- April 6, 1973      Analyzing Invisible Pollution-or More  
and More About Less and Less  
H. A. Laitinen  
at U. of I. Liberal Arts and Sciences  
Alumni Symposium  
The Ecology of Illinois-or What You  
Should Have Learned in Biology but  
Probably Didn't  
R. L. Metcalf
- April 13, 1973      Lead in the Environment  
H. A. Laitinen at Oklahoma State  
University
- April 24, 1973      Lead in the Environment  
H. A. Laitinen at Michigan State  
University
- May 30, 1973      Benefit-Risk Analysis and the Econo-  
mics of Toxic Substance Control  
G. Provenzano at USEPA Hazardous  
Materials Advisory Committee, Washing-  
ton, D. C.  
Ecosystem Modeling  
B. B. Ewing at USEPA Hazardous Materials  
Advisory Committee, Washington, D. C.
- June 30, 1973      Lead Transport and Periphyton Produc-  
tivity in a Small Polluted River  
H. V. Leland, and J. A. Baker  
36th Annual Meeting of the American  
Society of Limnology and Oceanography  
at Salt Lake City
- June 18, 1973      Localization of Lead Accumulation  
by Corn Roots  
C. P. Malone at annual meeting of  
the American-Canadian Society of Plant  
Physiology, Calgary, Alberta,  
Canada

June 20, 1973 and June 24, 1973	Calibration of CO <sub>2</sub> and Water Vapor Concentrations in a Semi-closed IRGA System F. A. Bazzaz (with R. W. Carlson) at AIBS meeting in Amhurst. The Influence of SO <sub>2</sub> and O <sub>3</sub> on Net Photosynthesis in Deciduous Tree Species R. W. Carlson
July 2, 1973	Lead in the Environment H. A. Laitinen at University of Alberta, Edmonton, Canada
August 7, 1973 to August 10, 1973	Automotive Emissions and Models for Transport and Distribution of Lead in the Environment G. L. Rolfe at NSF RANN Trace Contam- inants Conference, Oak Ridge The Uptake and Some Physiological Effects of Cadmium on Corn D. E. Koeppe, at same conference
August 27, 1973 to August 31, 1973	Laboratory Model Ecosystem Evaluation of the Chemical and Biological Behavior of Radiolabeled Micropollutants R. L. Metcalf at the FAO/IAWA/WHO "Symposium on Nuclear Techniques in Comparatives Studies of Food and Environmental Contamination" in Helsinki, Finland
August 28, 1973	Determination of Binding and Transport Constants of Metal Ions to Membranes D.F.S. Natusch at meeting of American Chemical Society in Chicago
October 8, 1973	Trace Metals in Airborne Particles D.F.S. Natusch at 3rd International Clean Air Congress, Dusseldorf, Germany
October 15, 1973	Interactions of Metal Ions with Membranes D.F.S. Natusch at Göttingen, Germany
October 18, 1973	Lung Deposition Profiles of Elements in Ambient Aerosols at Stockholm, Sweden

- October 23, 1973 Interactions of Metal Ions with Membranes  
D.F.S. Natusch at University of Oxford,  
Oxford, England
- October 25, 1973 Interactions of Metal Ions with Membranes  
D.F.S. Natusch at Mill Hill, London,  
England
- November 12, 1973 Lead Distribution in a Watershed Ecosystem  
G. L. Rolfe at Annual Meeting of the  
American Society of Agronomy, Las Vegas
- November 12, 1973 Concentration of Toxic Species in  
Submicron Size Airborne Particles;  
the Lung as a Preferential Absorption  
Site  
D. F. S. Natusch at symposium "Bio-  
medical Aspects of Air Pollution"  
Philadelphia, Penn.
- November 12, 1973 Conflicts in the Training of Graduate  
Environmental Chemists  
D.F.S. Natusch at symposium "Environ-  
mental Education for the Professional  
Chemist, New York
- December 2, 1973 What We Don't Know About Water Quality  
B. B. Ewing at a Department of Geology  
seminar, Western Illinois University.  
Lead Pollution in the Environment-  
or Leaded Gas and Leaded Grass  
B. B. Ewing at meeting of The Society  
of the Sigma Xi
- December 4, 1973 Analytical Techniques for Heavy Metals  
Other Than Mercury  
H. A. Laitinen at Vanderbilt University  
Nashville, Tennessee, at International  
Conference on "Heavy Metals in the  
Aquatic Environment"
- December 6, 1973 Environmental Lead Distribution in  
Relation to Automobile and Mine and  
Smelter Source  
Gary L. Rolfe at International Confer-  
ence on "Heavy Metals in the Aquatic  
Environment, Nashville, Tennessee

December 7, 1973 Risk-Benefit Analysis and the Economics of Heavy Metals Control  
G. Provenzano at International Conference on "Heavy Metals in the Aquatic Environment", Nashville, Tennessee

December 7, 1973 Animal Tissue Analysis by Nondestructive Methods  
Ruth Ernsberger at Analytical Chemistry Seminar Series

### Meetings Attended

October 23, 1972 Members of the Modeling Team attended  
to the International Symposium on Systems  
October 27, 1972 Engineering and Analysis at Purdue University

December 2, 1972 A. M. Hartley attended a meeting of  
to Subcommittee 1, Intersociety Committee,  
December 4, 1972 as American Chemical Society Representative, in Las Vegas

February 27, 1973 Govindjee attended the annual meeting  
to of the Biophysical Society in Columbus,  
March 2, 1973 Ohio

March 5, 1973 A. M. Hartley and R. S. Vogel attended  
to the Pittsburgh-Cleveland Meeting of the  
March 7, 1973 Society of Applied Spectroscopy; R. S. Vogel also attended the meeting of the Governing Board of the Federation of Analytical Chemistry and Spectroscopy Societies as representative of the Society for Applied Spectroscopy and also attended the meeting of the Governing Board of the Society of Applied Spectroscopy

March 1, 1973 G. Rolfe and F. Bazzaz attended the  
to Ecosystem Modeling Symposium in Athens,  
March 3, 1973 Georgia

March 28, 1973 R. J. Miller and D.F.S. Natusch attend-  
to ed the CSU meeting on Soils Pollution  
March 30, 1973 by Lead



March 12, 1973 to March 16, 1973	D.F.S. Natusch attended the UCLA Membrane Conference held at Squaw Valley, California
May 29, 1973 to May 30, 1973	B. B. Ewing and G. Provenzano attended the monthly meeting of USEPA Hazardous Materials Advisory Committee, Washington, D. C.
May 14, 1973 to May 16, 1973	D.F.S. Natusch attended the 3rd Annual Symposium on Analytical Chemistry of Pollutants at the University of Georgia
May 17, 1973	D.F.S. Natusch attended the Symposium on Trace Element Analysis of Coal, Fly Ash, Fuel, Oil, and Gasoline sponsored by EPA and NBS at Triangle Park, N.C.
June 12, 1973 to June 14, 1973	G. L. Rolfe, W. von Fischer, A. M. Hartley, D.F.S. Natusch, and R. S. Vogel attended the 7th Annual Conference on Trace Substances in Environmental Health at the University of Missouri, Columbia
June 18, 1973 to June 25, 1973	F.A. Bazzaz and Maarib Bazzaz attended the AIBS meeting in Amhurst. Dr. Bazzaz chaired a session on "Environmental Impacts" at this meeting
August 7, 1973 to August 10, 1973	H. A. Laitinen, G. L. Rolfe, A. M. Hartley, F. A. Bazzaz, D. E. Koeppe, G. Provenzano, G. L. Wheeler, and W. von Fischer attended the First Annual NSF-RANN Trace Contaminants Conference at Oak Ridge National Laboratory
August 27, 1973 to August 31, 1973	R. L. Metcalf attended the FAO/IAWA/WHO "Symposium on Nuclear Techniques in Comparative Studies of Food and Environmental Contamination" as an official U.S. delegate in Helsinki, Finland
November 11, 1973 to November 14, 1973	G. L. Rolfe attended the annual meeting of the American Society of Agronomy in Las Vegas, Nevada



November 18, 1973      H. A. Laitinen attended the NSF-RANN  
                          to      Symposium in Washington, D. C.  
 November 20, 1973

December 4, 1973      H. A. Laitinen, G. L. Rolfe and G.  
                          to      Provenzano attended the International  
 December 6, 1973      Conference on "Heavy Metals in the  
                          Aquatic Environment" at Vanderbilt Univ.

### Publications

- "Modeling Lead Pollution In a Watershed - Ecosystem"  
 by Gary L. Rolfe, Amar Chaker, John Melin, and  
 Ben B. Ewing, J. ENVIRON. SYS., Vol. 2(4),  
 December 1972, (pages 339-349)
- "Localization of Lead Accumulation by Corn Roots"  
 by C. P. Malone, D. E. Koeppe, and R. J. Miller,  
 PLANT PHYSIOLOGY 51, Supplement 115, 1973
- "Factors Affecting Distribution of Lead and Other  
 Trace Elements in Sediments of Southern Lake Michigan"  
 by H. V. Leland, S. S. Shukla, and N. F. Shimp  
 in "Trace Metals and Metal-Organic Interactions in  
 Natural Waters" by P. C. Singer of University of  
 Notre Dame (Published by Ann Arbor Science Publishers,  
 Inc.)
- "Heme-Synthesizing Enzymes and Urinary  $\delta$ -Aminolevulinic  
 Acid in the Rat" by R. L. C. Kao and R. M. Forbes in  
 PROCEEDINGS OF THE SOCIETY FOR EXPERIMENTAL BIOLOGY  
 AND MEDICINE 143, 1973 (pages 234-237)
- "Lead and Vitamin Effects on Heme Synthesis" by R. L. C.  
 Kao and R. M. Forbes in ARCHIVES OF ENVIRONMENTAL  
 HEALTH 27, 31-35, July, 1973
- "Study of the Interaction of Lead with Corn Root Exudate-  
 A Pulse Polarographic Study" by R. R. Gadde and H.A.  
 Laitinen in ENVIRONMENTAL LETTERS 5(2), 91-102 (1973)
- "Heavy Metals: A review of lead" by S. S. Shukla and H.  
 V. Leland in JOURNAL WATER POLLUTION CONTROL FED  
45 (6) June 1973, 1319-31

- "Trace Metals in Airborne Particulates" by D.F.S. Natusch, R. M. Davison, R. E. Lamb, J. R. Wallace and C. A. Evans, Jr., Proc. 3rd International Clean Air Congress, 1973
- "Toxic Trace Elements: Preferential Concentration in Respirable Particles" by D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr., SCIENCE 183, No. 4121, 1974 (pages 202-204)
- "Lead Distribution in a Central Illinois Woodland", by G. L. Rolfe, FORESTRY RESEARCH REPORT, No. 73-5, 1-2, October 1973
- "Study of the Sorption of Lead by Hydrous Ferric Oxide" by R. R. Gadde and H. A. Laitinen, ENVIRONMENTAL LETTERS, 5(4), 223-235 (1973)
- "Analytical Methods for Trace Metals: An Overview", by H. A. Laitinen, ANNALS OF THE NEW YORK ACADEMY OF SCIENCES, 199, 173-181, (1972)
- "Lead Outputs in Streamflow from a Watershed Ecosystem" WATER RES. BULL., 9:372-375 (1973)
- "The Effect of Cadmium on Electron and Energy Transfer Reactions in Corn Mitochondria", by R. J. Miller, J. E. Bittell, and D. E. Koeppe, PHYSOLOGIA PLANT, 28, 166-171 (1973)
- "Effects of Cadmium Nitrate on Spectral Characteristics and Light Reactions of Chloroplasts" by Maarib Bakri Bazzaz and Govindjee, ENVIRONMENTAL LETTERS, 6(1), 1-12 (1974)
- "Effects of Lead Chloride on Chloroplast Reactions" by Maarib Bakri Bazzaz and Govindjee, ENVIRONMENTAL LETTERS, 6(3), 175-191 (1974)
- "An Inexpensive Water Sampler for Monitoring Water Quality, J. M. Edgington, and G. L. Rolfe, FOR. RES. REP., No. 74-2, Univ. of Ill., Agr. Expt. Stal. (1974)

Papers Submitted for Publication

- "Differing sensitivity of corn and soybean photosynthesis and transpiration to lead contamination", by F. A. Bazzaz, G. L. Rolfe and P. Windle, J. ENVIRON. QUALITY
- "Effect of Cd on photosynthesis and transpiration of excised leaves of corn and sunflower", by F. A. Bazzaz and G. L. Rolfe, PHYSIOL. PLANT
- "Inhibition of corn and sunflower photosynthesis by lead", by F. A. Bazzaz, G. L. Rolfe, and R. W. Carlson, SCIENCE
- "The effect of heavy metals on plants: Part I. Inhibition of gas exchange in sunflower by Pb, Cd, Ni and Tl", by F. A. Bazzaz, Roger W. Carlson and G. L. Rolfe, ENVIRON. POLLUTION
- "Lead Halides and Automobile Exhaust Particulates: Some Properties of Environmental Significance", by Kenneth W. Boyer and H. A. Laitinen, ELECTRO-CHEMICAL SOCIETY
- "Polynuclear Aromatic Hydrocarbons in Automobile Exhaust Particulates", by Kenneth W. Boyer and H. A. Laitinen, SCIENCE
- "The effect of heavy metals on plants: Part II. Net photosynthesis and transpiration of whole corn and sunflower plants treated with Pb, Cd, Ni, and Tl" by Roger W. Carlson, F. A. Bazzaz, and G. L. Rolfe, ENVIRON. RESEARCH
- "Studies of Heavy Metal Adsorption by Hydrous Oxides" by R. Rao Gadde and Herbert A. Laitinen, ANALYTICAL CHEMISTRY
- "Lead Contamination of Soils and Plants Along Highway Gradients in East-central Illinois", by Alan Haney, Joyce A. Carlson, and Gary L. Rolfe, TRANS. ILL. ACAD. SCI.
- "Analytical Techniques for Heavy Metals Other Than Mercury", by H. A. Laitinen, (Proceedings of International Conference on Heavy Metals in the Aquatic Environment, Vanderbilt University - 1973)

- "Localization of Lead Accumulated by Corn Plants", by Carl Malone, D. E. Koeppe, and Raymond J. Miller, PLANT PHYSIOLOGY
- "Lead in insects: Evidence for biological concentration", by P. W. Price, B. J. Rathcke and D. A. Gentry, ENVIRONMENTAL ENTOMOLOGY
- "Risk-Benefit Analysis and the Economics of Heavy Metals Control", by G. Provenzano (Proceedings of International Conference on Heavy Metals in the Aquatic Environment, Vanderbilt University - 1973)
- "Effects of Lead Contamination on Transpiration and Photosynthesis of Loblolly Pine (Pinus taeda L.) and Autumn Olive (Elaeagnus umbellata Thunb.), FOREST SCIENCE by Gary L. Rolfe
- "Environmental Lead Distribution in Relation to Automobile and Mine and Smelter Source", by G. L. Rolfe and J. C. Jennett (U. of Missouri), (Proceedings of International Conference on Heavy Metals in the Aquatic Environment, Vanderbilt University - 1973)
- "Lead Distribution in Tree Rings", by G. L. Rolfe, FOREST SCIENCE
- "A Compartment Model of Lead Uptake in Juvenile and Adult Rats", by G. L. Wheeler and J. Abdelnour
- "An Experimental Study of Ecosystem Stability in a Controlled Environment" by G. L. Wheeler and A. G. van der Valk (Iowa State U)
- "Applications of a Mercury Plated Graphite Electrode in Anodic Stripping Voltammetry", by A. M. Hartley and D. Devine (presented at the 8th Great Lakes Regional Meeting - American Chemical Society, West Lafayette, Indiana, 1974), JOURNAL OF ELECTRO-ANALYTICAL AND INTERFACIAL CHEMISTRY
- "Signal Characterization and Measurement in Micro-sample Atomic Absorption Spectrophotometry", (presented at the 7th Materials Research Symposium, National Bureau of Standards, October, 1974, Gaithersburg, MD), by R. S. Vogel and A. M. Hartley, JOURNAL OF APPLIED SPECTROSCOPY



## Dissertations

### Ph.D.

Will B. Betchart: "Optimum Sample Intervals for Water Quality Monitoring"

Kenneth W. Boyer: "Analysis of Auto Exhaust Particulates"

Race Li-Chan Kao: "Lead Toxicity in Experimental Animals"

George Provenzano: "The Economics of Environmental Quality Management: A General Systems Approach"

Gary L. Rolfe: "Lead Uptake of Selected Tree Seedlings"

Noel Watkins: "Cathodic Stripping Coulometry of Lead"

### M.S. Theses

John McNurney - "Benthic Invertebrates as Indicators of Lead Pollution in a Stream Ecosystem" - Special Problem Report - Environmental Engineering

L. L. Bonen - (student of G. L. Jendrasiak) "The Interaction of Lead Chloride with the Erythrocyte Membrane and Membrane Lipids"

J. A. Baker - "Aufwuchs Accrual and Lead Incorporation in a Small Polluted River" (student of H. V. Leland)

### F. GRANTEE - USER CONTACTS

During the course of the report period contacts have been made with the following individuals, agencies, and/or companies:

World Health Organization

U.S. Environmental Protection Agency

Illinois Environmental Protection Agency

Illinois Institute for Environmental Quality

Illinois Pollution Control Board

Illinois Department of Public Health

Illinois Department of Transportation, Division of  
Highways

Illinois Fertilizer and Chemical Association

Champaign-Urbana Public Health District

International Lead Zinc Research Organization, Inc.

E. I. duPont de Nemours & Co., Inc.

Ethyl Corporation

Universal Oil Products

Argonne National Laboratory

Anderson, Indiana Air Pollution Control Agency

National Institute for Environmental Health Sciences

National Cancer Institute

#### Utilization of Benefit-Risk Analysis Research

The conceptual development of benefit-risk analysis has generated potential user interest on the part of a number of individuals and organizations. Benefit-risk analysis is an analytical framework for (1) evaluating the economic benefits associated with the use of toxic substances or heavy metals; (2) assessing the risks of environmental



damages from toxic substances or heavy metal waste discharges; and (3) comparing the benefits with the risks in a decision making context.

This research was initially stimulated by a request for a presentation (May 29, 1973) before the Hazardous Materials Advisory Committee for the U.S. Environmental Protection Agency. The request came from Dr. Winfred F. Malone, USEPA, and Staff Science Advisor to the Committee. As a result of this presentation several contacts have been made with individuals who are interested in applying benefit-risk analysis to environmental management decisions. The following is a partial list of these individuals.

(1) Within the U.S. Environmental Protection Agency

Dr. Alan P. Carlin, Director  
Implementation Research Division  
Office of Research and Development  
Washington Environmental Research Center

Dr. Fred Abel and Dr. Dennis Tihansley  
Economic Analysis Branch  
Implementation Research Division  
Office of Research and Development  
Washington Environmental Research Center

Dr. Robert Horton  
Senior Research Advisor  
Office of the Director  
National Environmental Research Center  
Research Triangle Park, North Carolina

Mr. Thomas Waddell  
Office of the Director  
National Environmental Research Center  
Research Triangle Park, North Carolina

Dr. Don Gillette  
Dr. Ken Bridbord  
Dr. Doug Hamner  
Epidemiology Branch  
Human Studies Laboratory  
National Environmental Research Center  
Research Triangle Park, North Carolina

Mr. David Patrick  
Mr. William Hamilton  
Cost Analysis Branch  
Strategies and Air Standards Division  
Office of Air Programs  
Research Triangle Park, North Carolina

Dr. Mike Prival  
Miss Doris Roupp  
Office of Toxic Substances  
Washington, D. C.

Mr. Allan Richardson  
Criteria and Standards Division  
Office of the Assistant for Categorical  
Programs  
Washington, D. C.

(2) Within the National Research Council

Dr. Raphael Kasper and Mr. Ron Tipton  
Committee on Social and Economic Costs  
and Benefits of Automobile Emissions Controls  
Environmental Studies Board  
National Research Council  
Washington, D. C.

(3) Within the U. S. Congress

The Honorable Joseph R. Biden, Jr., Chairman  
Panel on Environmental Science and Technology  
Subcommittee on Environmental Pollution  
Committee on Public Works  
U.S. Senate  
Washington, D. C.

The Honorable Edmund S. Muskie, Chairman  
Subcommittee on Environmental Pollution  
Committee on Public Works  
U.S. Senate  
Washington, D. C.

Mr. Leon G. Billings  
Senior Staff Member  
Subcommittee on Environmental Pollution  
Committee on Public Works  
U.S. Senate  
Washington, D. C.

Mr. Michael B. Brownlee  
Staff Counsel  
Subcommittee on Environment  
Committee on Commerce  
U. S. Senate  
Washington, D. C.

(4) Other Interested Parties

Mr. David Schoenbrod  
Natural Resources Defense Council, Inc.  
15 West 44th Street  
New York, New York







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